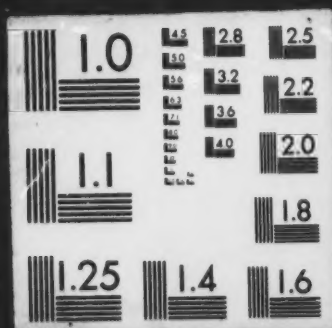


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SOLID WASTE CONVERSION: CELLULOSE LIQUEFACTION

WORCESTER POLYTECHNIC INSTITUTE

PREPARED FOR
NATIONAL ENVIRONMENTAL RESEARCH CENTER

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SOLID WASTE CONVERSION:
CELLULOSE LIQUEFACTION

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report provides an extensive survey of the state-of-the-art in cellulose liquefaction and its chemistry. The process concept is detailed and related to pyrolysis.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

This final report documents the activities on the Solid Waste Liquefaction Project. In the course of this project, the stage has been set to proceed with the experimentation that will be necessary for scaling the process up to a practical commercial level. The report provides an extensive survey of the state of the art in cellulose liquefaction and its chemistry, and the process concept is detailed and related to pyrolysis. In essence the whole purpose of this hydrogenation study was to produce Btu's. Material with a heating value close to that of wood (5000 cal/gm) was used to make an oxygen, nitrogen, and sulfur free oil having a useful heating value in the vicinity of 10,000 cal/gm.

This cellulose liquefaction process is in effect a continuous hydrocracking process, based on technology which is readily available from the petroleum industry, although not previously applied to solid waste. The process envisioned uses a carrier oil in which the solid waste feed (in our case, sewage sludge, polystyrene, and powdered newspaper) is slurried. The advantage of using an oil carrier, aside from the obvious point that it provides a means for pumping solid matter into a flow reactor, is that a liquid reaction medium is present which (unlike water) does not present a critical temperature problem and the attendant requirement of high operating pressures. Water plays an intrinsic part in the reaction for the in-situ production of hydrogen.

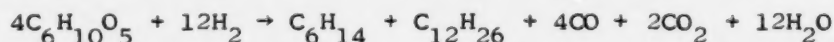
Equilibrium calculations indicate that hydrogen (rather than carbon monoxide) is the preferable reactant gas. When carbon monoxide is the reactant gas, char or carbon always will be present at equilibrium.

This report describes the nearly complete conversion of polystyrene, newspaper and sewage sludge in batch studies and the screening of process

variables in a continuous stirred tank reactor (CSTR) system.

The effects of catalyst, temperature, pressure, and reaction time were correlated and catalyst optimized by simple batch and continuous experimentation. The continuous unit was brought on stream and operated at the optimal conditions suggested by the batch experimentations. The operations of the continuous unit provided valid material balances and a clearer understanding of the meaning of batch data.

Using 20% powdered newspaper slurried in mineral oil as a feed stock, conversions as high as 95% have been obtained in batch experiments and about 85% in the CSTR. A catalyst screening study has shown nickel to be an optimum catalyst. The hydrocarbon oil produced has a low oxygen content ($<5\%$) and a high heating value (8,300-10,000 cal/gm) suggesting that it is equivalent to petroleum-derived fuel. CSTR reactor conditions studied were in the range 400-460°C, 34-70 atm., 2-5 LHSV, and 11 to 40 minutes space time. Water-gas shift and synthesis gas reactions occur producing hydrogen in-situ and reducing by almost 50% the amounts of externally produced hydrogen that would otherwise be required. A crude approximation of the stoichiometry is



This is equivalent to a production of 2-1/4 Bbl oil/ton dry organic solid waste.

The data from the continuous reactor were used to make economic projections for a 36 ton/day unit, which would be suitable for processing the organic solid waste from a town. A scale up design study for processing solid waste from Holden, Mass. is presented.

This report was submitted in fulfillment of Grant Number R-EP-00516 (800 688) by Worcester Polytechnic Institute under sponsorship of the Environmental Protection Agency. Work was completed as of June 30, 1973.

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CONCLUSIONS

1. Computer-based equilibrium calculations indicate that a) hydrogen, rather than carbon monoxide, is the preferred reactant gas, b) a high partial pressure of hydrogen and the presence of water is needed to suppress char formation, and c) the yield of liquid hydrocarbons decreases with increasing temperature.
2. An oil carrier is the most suitable reaction medium. An aqueous medium restricts the operating temperatures and produces excessive pressures. The addition of water to the oil carrier thickens the newspaper slurry and renders pumping quite difficult.
3. Initial experiments with a high pressure differential scanning calorimeter suggest the possible feasibility of this technique as a means of catalyst screening and microscale reaction study.
4. Hydrogenation of ground dried sewage sludge using a nickel on kieselguhr catalyst at temperatures in excess of 400°C produced a high quality liquid fuel at high conversion (92%). At lower temperatures (370°C) the inorganic impurities in the sewage sludge exhibited catalytic activity.
5. Preliminary studies on the liquefaction of industrial polystyrene waste indicate that at temperatures above 427°C , even in the absence of hydrogen, conversion to liquid and gaseous products in excess of 95% can be achieved.

6. It was concluded from batch studies using powdered newspaper as a solid feed that a) a high quality (low oxygen, 8,900-10,000 cal/gm) oil could be prepared and b) metal catalysts must be either reduced prior to use or be reducible under in situ reaction conditions to be effective for the liquefaction process.

7. The production of bituminous materials in low severity experiments (316°C) using the continuous stirred tank reactor (CSTR) suggest the advantage of higher temperatures for eliminating this bitumen stage and producing liquid fuels.

8. In the continuous liquefaction of powdered newspaper, the yield of oil is enhanced by increasing both hydrogen pressure (to 70 atm) and temperature (to 460°C) while restricting space time to 15.1 minutes (to reduce gasification). Under these conditions, a yield of 46.1 grams of oil (per 100 grams of newspaper fed) was achieved.

9. The carrier oil plays a key role in the reaction process, possibly by a) solubilizing cellulose degradation products for subsequent hydrogenation, b) acting as a reaction medium, and c) transporting carbohydrate fragments to active metal sites.

10. The water gas shift reactions were found to be valuable sources for the in-situ production of hydrogen. Estimates suggest that 50% of the hydrogen gas requirements in our experiments were supplied by this in-situ process.

11. Process scale-up studies project that a 1000 ton per day solid waste liquefaction plant can break even if the product oil sells for \$4.75 per barrel.

RECOMMENDATIONS

1. Although nickel catalysts have been found effective, further catalyst studies should be performed to minimize catalyst costs and optimize product yields. A process for recovering and recycling catalyst should also be developed if disposable materials are not available.
2. The thermodynamics and kinetics of the water-gas shift gas reactions that are proceeding in situ in the liquefaction process should be studied further in an effort to totally eliminate, or at least minimize, the size of a hydrogen plant for the process.
3. Particle size studies, both CSTR and batch experiments, should be made to evaluate the economics of the available grinding equipment and assess the importance of grinding costs compared to those of the overall process.
4. Hydrotreating processes should be tested for post-treatment of the product oil in order to upgrade it to a more efficient fuel - e.g., reduce bromine number, modify viscosity, pourability, and flash point.
5. Feed stocks other than powdered newspaper, polystyrene, and sewage sludge should be tested for feasibility of being converted to oil - e.g., plastics, manure, wood, sawdust, garbage, leaves, and grass, as well as other types of organic waste material.
6. The cellulose liquefaction process has been shown to be a practical one. However, only speculations have been made regarding the theory behind it. Studies should be carried out to get a better idea of the stoichiometry, reaction paths, and kinetics. The knowledge gained from

these studies would have a profound influence on the type of final re-action system that is chosen for a commercial plant.

7. The process development studies should proceed to a level where the first scale up can be made - preferably in the 10 to 50 ton/day range. Data obtained at this level can then be used for optimal design of, e.g., 1000 ton/day municipal plants.

INTRODUCTION

THE SOLID WASTE PROBLEM

The problem of the inundation of the United States by solid waste should be considered in the context of the projection that, by the year 2000, or even earlier, we shall have exhausted our reserves of natural gas and petroleum and we shall be making massive inroads even into our coal reserves (1). What develops is, of course, the concept of resource recovery. We cannot continue to expend our resources indefinitely.

The concept "the solution to pollution is dilution" falls by the wayside. Mountains of waste and garbage cannot be accommodated - cannot be burned. Solid wastes must be converted to useful economical products. As an example, compressed refuse can be used for building blocks (2,3,4).

Since collection and transportation costs for waste cannot be eliminated, processing techniques that can return a useful product are a necessity. Our approach, in the context of the overall population growth, resource limitations, and ecology, is to convert waste to petroleum. We must manage our oil resources to accommodate the giant populations that are projected (5,6).

Quoting Philip H. Abelson in his recent editorial in Science Magazine (7)

"The public is aware of problems with respect to the environment, energy, balance of payments, and national security. However, there does not seem to be general awareness of the extent to which these problems are intertwined.

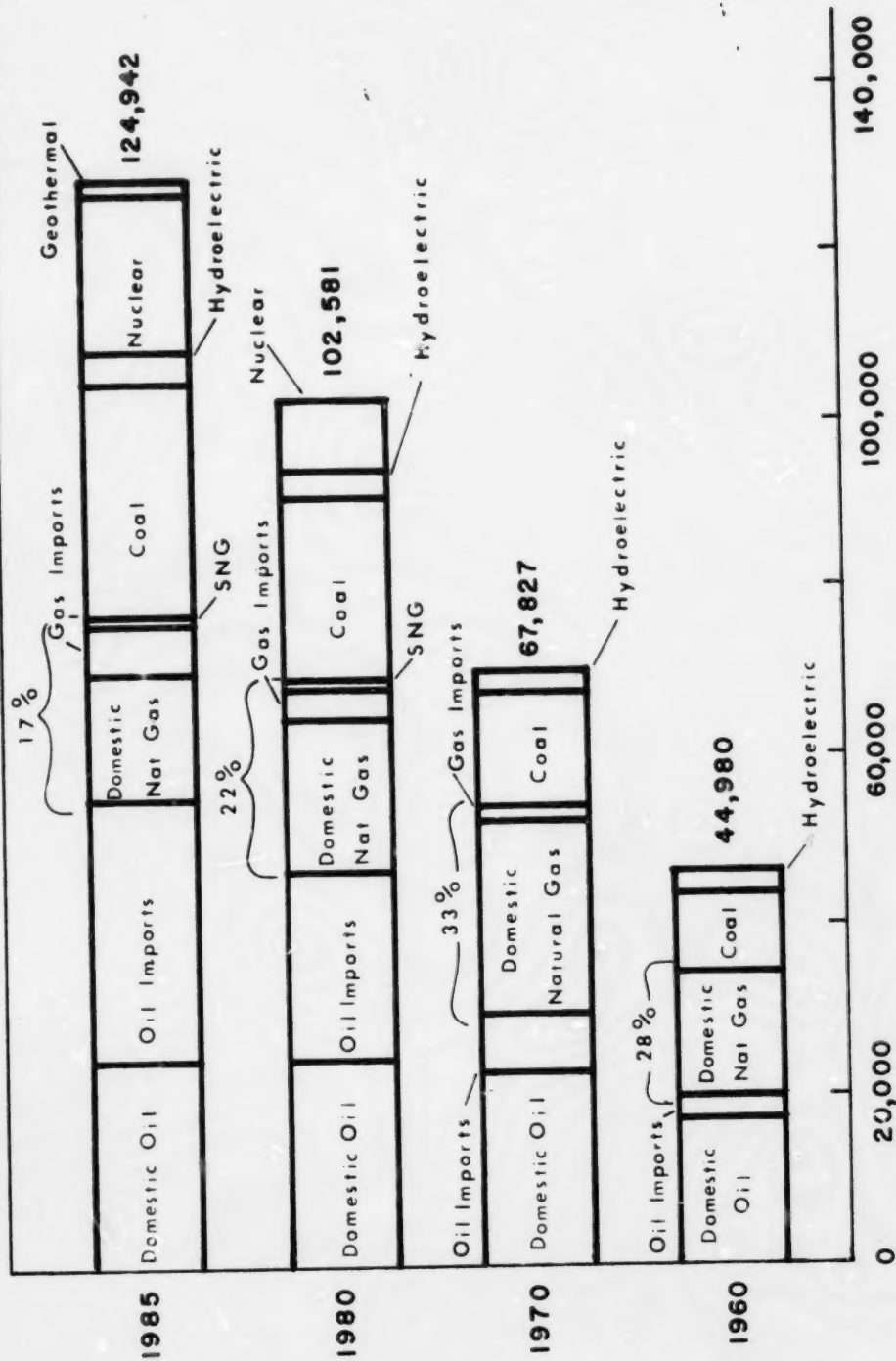
The demand for clean energy has continued to grow, while reserves of natural gas and petroleum have diminished. Imports of hydrocarbons have expanded sharply and seem destined to increase much more. Already these imports are responsible for much of our deficit in the balance of payments. Continuation of present trends must lead to much deeper deficits, more devaluation, and massive loss of confidence in the dollar. At the same time, we are becoming vulnerable to petroleum blackmail.

Our major, and perhaps most vital, source of energy is petroleum and its various refined products. These materials provide 44 percent of our energy needs, but reserves and producing capacity are falling. In 1957, during the Suez crisis, we were able to supply our own needs and much of Europe's. Today, about 25 percent of our needs are supplied from abroad, and imports are increasing rapidly. Last year, total consumption of petroleum and its products was 5,523 million barrels. Reserves in the 48 contiguous states dropped to about 28,000 million barrels. New discoveries during the year contributed a trifling amount.

A continuation of our present trends in the utilization of energy and in growing dependence on foreign sources must lead to problems of unprecedented magnitude. We must place more emphasis on finding means of curtailing energy consumption while moving vigorously to develop acceptable substitutes for oil and natural gas."

In the past, the U.S. has been a tremendous consumer of energy and, in all probability will continue to be one in the future. Figure 1 represents an estimate of the U.S. energy balance by 1985, provided that the economic conditions and government policies of June 1971 continue into the future (8). It is evident from Figure 2 that the use of energy in the U.S. will almost double in the period from the present until 1985. Where is this energy to come from? Certainly, domestic oil production cannot be expected to double in this 15 year period as oil reserves are depleted. Even the celebrated Alaskan North Shore oil reserves are expected only to postpone, but not solve, this problem. In fact, the demand for energy on just the West Coast of the U.S. is expected to keep pace with projected Alaskan Oil production and delivery capacity (9). Also, the people of the United States cannot expect to double oil imports as the energy appetite of the rest of the world grows at an even faster rate than ours.

The United States faces a growing problem due to its vast economic development: the adequate disposal and/or reuse of its urban and industrial refuse. Rivaling air and water pollution control in complexity



CONSUMPTION, TRILLION B.T.U.

Figure 1. Energy balance for the United States

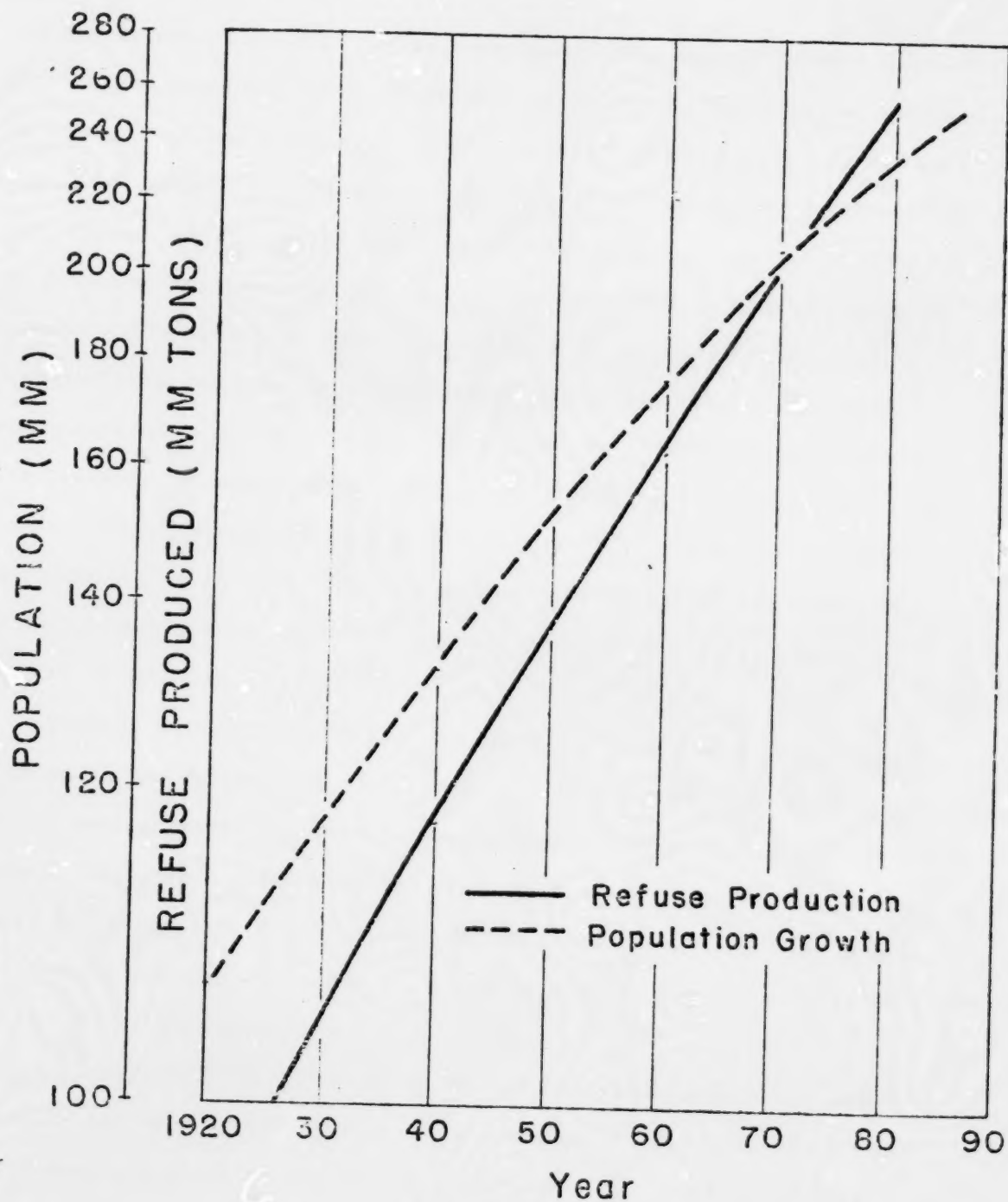


Figure 2. Population growth and refuse production versus year.

and importance, the urban refuse heap cannot be properly handled now and will become difficult to treat in the future due to the expected increase in personal living standards. A direct relationship exists between the degree of industrialization in a country and the amount and character of its refuse. It is ironic that rubbish of economic potential is totally discarded with little thought of its impact on the economy or the environment. This situation cannot be expected to last because it will eventually become profitable to recover the glass, metal, and other components of urban garbage and reuse them, as this planet's resources are limited. In other words, garbage is a potential resource and, unfortunately, as can be seen from Figure 2 (10), a readily accessible raw material which will soon be produced at a rate that outstrips the growth in population.

METHODS OF DISPOSAL

Present methods of disposal are ineffective and will become even more so in the future, due to the sheer volume of discarded materials. Refuse per capita is expected to increase much faster than population growth; therefore, more effective means of disposal should be explored now. Currently, the most popular and least effective technique is open air dumping and burning. This is a health hazard, and contributes to air and water pollution.

Sanitary landfill is an acceptable process when possible. Sanitary landfill and open dumping presently account for ninety percent of the solid waste disposal of the United States (11,12). Aside from open dumping, which is ecologically unacceptable, sanitary landfill is the least costly method (\$1.35-3.50/metric ton operating cost)(12). The

disadvantages are that rain tends to leach out certain substances and pollute the subsurface waters and that it is becoming more difficult to use as the amount of available (and suitable) land decreases and concern about the environment grows.

Incineration, the second most popular disposal method, is used by many large cities, where the volume of rubbish justifies the cost of such a device. There are 300 municipal incinerators operating in the United States, but they add to air pollution and only one-fourth of these systems meet current air codes (12,13,14).

Incineration operating costs range from \$5.50 to \$11.00 per metric ton (12). Recovering some of the energy by producing low pressure steam can reduce incineration costs by \$3.75 per metric ton (15). But, unless a specific need for low pressure steam exists, it is not economical to build such a steam plant. Thus, incinerators defeat the purpose of effectively recycling wastes.

Compacting garbage into building blocks was successfully accomplished and this method has some public appeal as a disposal technique. Composting is a generally uneconomical method of solid waste management. Over twenty composting plants have been built in the United States since 1951. All but two or three have been shut down by shortage of markets for the products and by technical difficulties (14). Operating costs of \$20 to \$30 per metric ton (12) make extensive use of this process prohibitive. It can be seen that inexpensive, effective, acceptable refuse disposal procedures will have to become available in the near future to meet the expected onslaught of discarded materials.

CHARACTERIZATION OF MUNICIPAL REFUSE

In order to better understand how to approach the municipal refuse problem, the composition of waste should be known. Table 1 (16) presents the physical composition of municipal solid wastes for several geographic locations with classifications given according to general material categories. As is obvious, paper products make up the bulk of municipal refuse with food wastes and metal and glass products as the other portions. Table 2 (16) is a summary showing percentage ranges for these various categories. From these tables we get an idea about the composition from a physical standpoint, but we are not provided with the details necessary to analyze the problem.

Perhaps a more useful way of classifying the refuse is by chemical makeup. Table 3 (17) shows the composition by major chemical type. From this data we may reasonably state that refuse can be considered to be made up of 50% cellulose, 20% moisture, 25% inorganics, and the remainder miscellaneous organics. It then follows that, after the removal of inorganics, possibly for reuse, the chemistry of the waste heap is the chemistry of cellulose.

CELLULOSE CHEMISTRY

Cellulose is the most widely distributed skeletal polysaccharide, amounting to approximately fifty percent of the cell-wall material of wood and plants. Some natural materials are practically pure cellulose, e.g. cotton. Cotton is α -cellulose, a form insoluble in 17.5% NaOH. Plant and wood celluloses generally contain β -cellulose as well, a material soluble in the indicated solution. Thus, although cellulose is formed from D-glucose building blocks joined by β -1,4-glucosidic bonds, there are differences in the degree and types of association within cellulose molecules.

Table 1. PHYSICAL COMPOSITION OF MUNICIPAL SOLID WASTES BY LOCATION
(percent by weight, wet basis)

Geographical Location	Paper products	Metal products	Glass products	Food wastes	Wood	Plastics, leather, rubber cloth, and synthetics
New Jersey	51	8	4	10	4	4
Illinois	42	9	6	14	-	-
Ohio	42	9	8	28	3	3
Arizona	43	10	8	22	2	1
California	54	7	2	15	2	2
Kentucky	--	9	6	11	-	-
New York	40	8	-	10	7	3
Tennessee	46	11	11	26	1	5

Table 2. MUNICIPAL SOLID WASTES: PHYSICAL CHARACTERISTICS DATA
(Typical Ranges)

Category	Percent by weight (wet basis)
Metal products	8-11
Glass products	8-11
Paper products	40-54
Food wastes	10-26
Yard wastes	3-80
Wood products	3-70
Plastic products	1-20
Cloth, rubber, leather, synthetics	1-20
Dirt, ashes, rocks, and other inerts Density = 200-500 lb per cu yd	1-50

Table 3. MUNICIPAL REFUSE COMPOSITION BY MAJOR CHEMICAL TYPES

Component	Wt. %
Moisture	20.73
Cellulose, sugar, starch	46.63
Lipids (fats, oils, waxes)	4.50
Protein	2.06
Other organic (plastics	1.15
Ashes, metal, glass, etc.	24.93

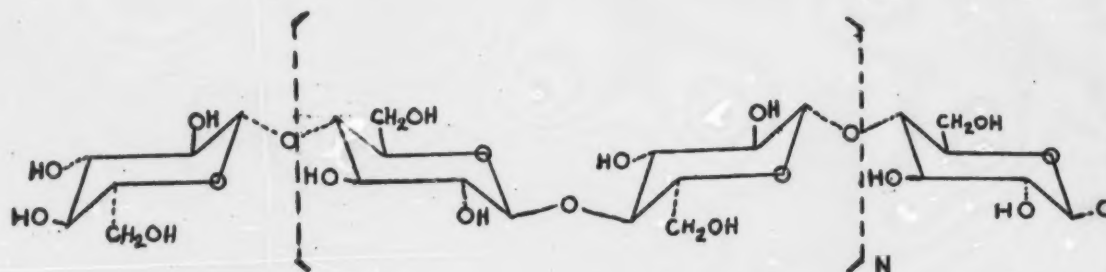
Wood cellulose occurs in the presence of hemicellulose of related structure and with lignin, a nonpolysaccharide. Wood also contains oleoresins, which are commercially extracted and steam distilled to produce turpentine and rosin (naval stores). Wood chemistry, then, is significantly more complex than α -cellulose chemistry.

The cellulose molecule is a polymer with molecular weight generally in the range of 300,000 to 500,000. Table 4 shows typical materials and their degree of polymerization.

Table 4. CELLULOSE CHARACTERISTICS (1B)

Source	Molecular Weight	Degree of Polymerization
Native Cellulose	600,000 - 1,500,000	3,500 - 10,000
Chemical Cottons	80,000 - 500,000	500 - 3,000
Wood Pulp	80,000 - 340,000	500 - 2,100
Rayon Filament	57,000 - 73,000	850 - 450

If one considers conformational analysis, in which anhydroglucopyranose units are in the chair form, the structure is as follows:



Note the manner in which cellulose is built from glucose units. Glucose, as well as cellobiose, cellotriose, and cellotetrose can be isolated when cellulose is hydrolyzed. Complete hydrolysis by acid yields D-(+)-glucose as the only monosaccharide.

In general, other polysaccharides also occur in the presence of cellulose. For example, cereal straws and bran contain pentosans (most commonly xylan, which is built up from d-xylose units) which yield pentoses on hydrolysis, rather than glucose. Starch is present in the majority of plants, and this material is built up from maltose units.

The cellulose molecule is thread-like, existing as fibrils - long bundles of molecules stabilized laterally by hydrogen bonding between hydroxyl groups of adjacent molecules. Molecule arrangement in the fibrillar bundles is so regular (but not perfect) that cellulose has a crystalline X-ray diffraction pattern. Hydrogen bonding and the arrangement of the cellulose molecules in native cellulose, taken from Liang and Marchessault (19) is shown on Figure 3. An excellent discussion and bibliography of review articles on this subject is provided by Ward (20). He points out that the consequence of the high degree of order in native cellulose is that not even water molecules, let alone enzymes, can enter the structure. Consequently, native cellulose is inert in the digestive tract. The structure of acid or alkali swollen cellulose is open; and this material is readily split by cellulase. Table 5 lists compositions of wood hydrolyzates (21).

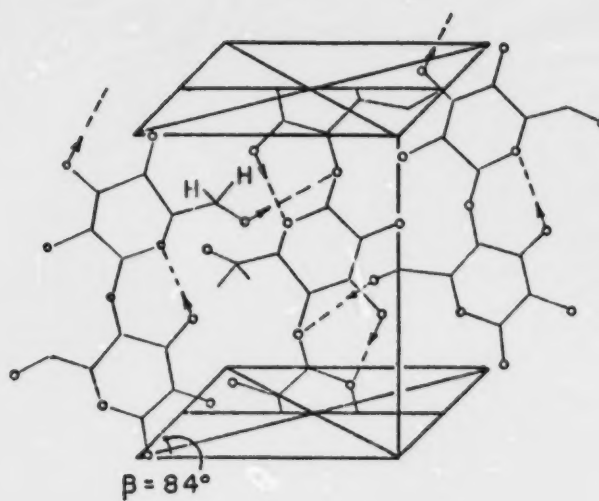


Figure 3

Structure in Native Cellulose

Table 5. COMPOSITION OF THE TOTAL HYDROLYZATE OF WOOD(21)

	Birch %	Jack Pine %
Glucose	67.7	67.6
Mannose	1.8	14.1
Galactose	0.0	6.2
Fructose	---	---
Xylose	30.1	8.9
Arabinose	<u>0.4</u>	<u>3.2</u>
	100.0	100.0

THERMAL REACTIONS OF CELLULOSE TO PRODUCE FUEL

With the advent of municipal solid waste disposal problems, cellulose pyrolysis technology is currently being revitalized. We are all familiar with the use cellulose has as an energy source. Wood has been a fuel since time immemorial. Unfortunately, the moisture content of wood is generally high - typically 50% - and this detracts from its heating value, since heating value decreases linearly with moisture content.

Pyrolysis technology for upgrading cellulose to a more efficient fuel is also ancient. Carbonization of hard wood to charcoal is probably the world's first chemical process, and it enabled cave men to have a smokeless fuel for inside utilization. Typical hardwood yields as wt. % obtained by retorting are charcoal 25.2, methanol 1.9, acetic acid 2.9, tar and oil 5.0, gas 18.3, and water 46.7. Shreve (22) provides these figures as well as process descriptions of both hardwood distillation and the naval stores industry, which is based on soft woods. Charcoal is an

unimportant energy source at present, having limited use for iron smelting and as a cooking fuel.

The heating value of cellulose fuels does not approach that of fossil fuels. For example, dried wood or bagasse is typically 4,440-5,000 cal/gm. This can be compared to heating values of fuel oil, coke, and bituminous coal - approximately 10,600, 7,210, and 8,430 cal/gm., respectively (23).

In addition to bagasse, other cellulosic materials besides wood are burned directly for their heating value. Municipal and industrial solid waste, black liquor, coffee grounds, rice hulls, and furfural residue are examples of fuels that have been used for steam generation from waste heat boilers (23).

The heating value of the overall refuse is 2760 cal/gm. while that of the moisture and ash free portion is 5070 cal/gm. Rosen et al. (10) project a yield structure from total municipal refuse of 22.5% char, 19.5% organic liquids, and 13.5% gas with the pyrolysis processing scheme shown on Figure 4. They calculate that the pyrolysis process is technologically and economically feasible for pursuit by a municipality, in spite of the fact that the liquid and gas produced are only marginally suitable as fuels. Mallan (24) has reported the following pyrolysis yields and heating values from oven-dried shredded municipal refuse: 35 wt.% char at 5050 cal/gm.; 40 wt.% oil at 6740 cal/gm.; 10 wt.% gas at 5350 cal/liter. The oil fraction contains 20 wt.% oxygen making it unsuitable for normal uses except for blending at low levels into Bunker C. The char has no economic use at present and would have to be landfilled.

The low heating values of cellulose and their pyrolysis products are due to high oxygen contents. Table 6 lists the heating values of fuels with varying oxygen content. Higher heating values result from fuels of lower oxygen content, and the most useful domestic and industrial

REFUSE PYROLYSIS PLANT

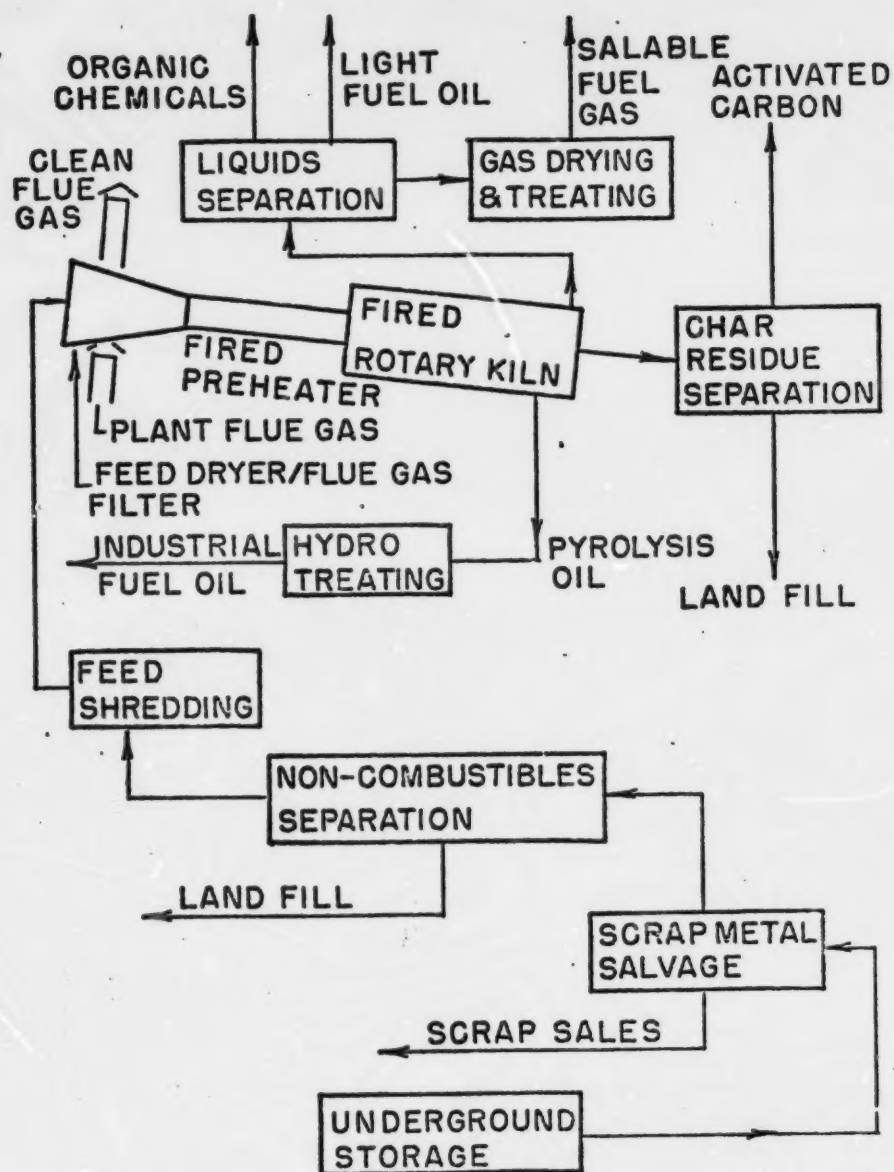


Figure 4

fuels (i.e., those that burn with the highest flame temperature) are oxygen-free hydrocarbons. Thus, pyrolysis has disadvantages because of the low heating value of the oil and because of the fact that char is not useful. Pyrolysis is, in effect, a process for producing an unwanted product (char) from an equally unwanted raw material (solid waste).

Table 6. HEATING VALUES OF SOME FUELS OF DIFFERENT OXYGEN CONTENT (25)

Fuel	Oxygen Content %	Cal/gm
Wood	41.0	4,950
Peat	30.3	5,080
Lignite	18.3	6,220
Subbituminous Coal	16.2	6,780
Bituminous Coal	6.1	8,080
WPI Product Oil	1-5	9,830-10,300
Octane	0.0	11,400
Methane	0.0	13,100

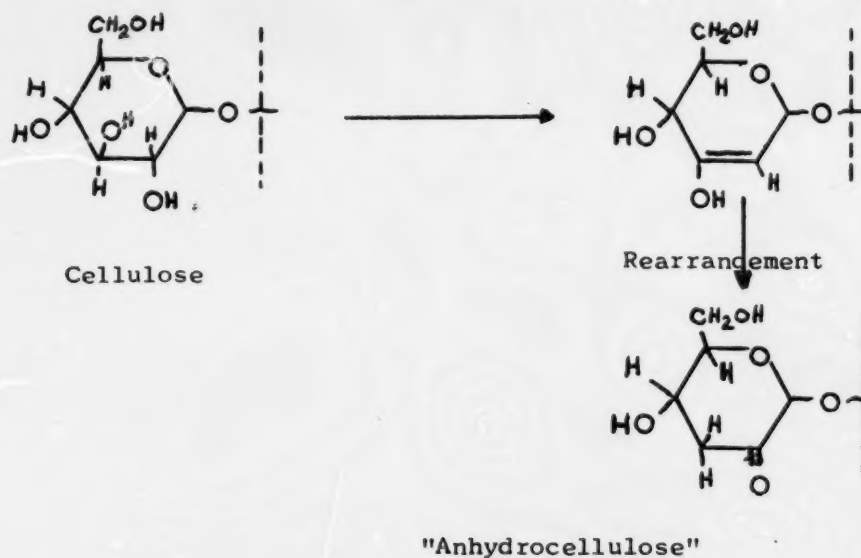
High temperature decomposition of cellulose has been studied since the beginning of this century and an extensive amount of literature is available (26). The primary reaction during the thermal decomposition of cellulose is carbonization with the elimination of water and carbon dioxide. Other products e.g., tar, organic acids, etc. are formed by secondary, tertiary, and further reactions.

The recent crisis in solid waste disposal and growing interest in resource recovery have prompted renewed studies of the mechanism and chemistry of the pyrolysis process. Several investigators (27-34) independently have arrived at more or less similar results, using thermo-analytical techniques to study thermal decomposition of cellulose.

Arseneau (33) in his most recent studies (1971) suggested the following steps in cellulose pyrolysis:

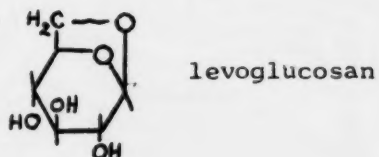
1. Dehydration (Endothermic) of a part of cellulose occurs at about 210°C, producing "Anhydrocellulose" which further undergoes secondary reactions (Exothermic) giving rise to CO, CO₂, H₂O and char.

By Infrared analysis the presence of C=O and C=C bonds were detected and he proposed the following scheme:



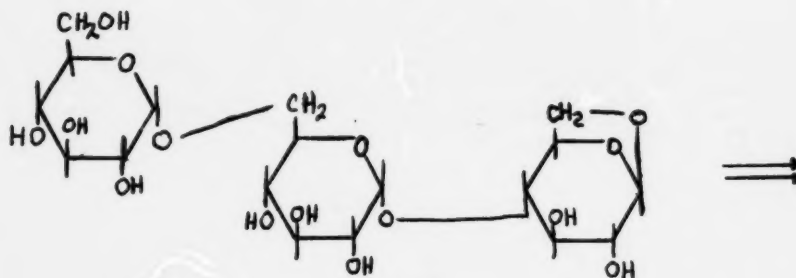
Browne (34) made the same observation but suggested that instead ketenes (C=C=O) were produced and were responsible for the C=C and C=O bonds detected by Arseneau.

2. Depolymerization of the residual cellulose occurs at about 270°C and results in tar formation (in which levoglucosan, 1,6 anhydroglucopyranose, is an intermediate). Depending on the reaction conditions the levoglucosan may either volatilize (Endothermic) or decompose thermally (Exothermic) to evolve gases and a carbonaceous material (char). These two reactions are "competitive".



Formation of levoglucosan occurs by scission of the 1,4,glycosidic linkages (of the cellulose) followed by intramolecular rearrangement. When levoglucosan was distilled it yielded reaction products similar to those obtained by destructive distillation of cellulose (31), thereby lending weight to the argument that levoglucosan is an intermediate of this reaction. Since levoglucosan is also produced from the destructive distillation of glucose (35), it can be speculated that glucose is formed initially from cellulose decomposition and then the glucose dehydrates in secondary reactions to produce levoglucosan.

Carvalho et al., have shown (36) that levoglucosan, like other glucosans, tends to undergo polymerization to give polyanhydro glucose.



The polymerization products of levoglucosan were dextrans (dimeric to octameric products). These dextrans produced were amber colored, brittle resins, completely water soluble and free of gel. The ring conformation of dextrans is more stable than that in the levoglucosan.

Cellulose paper of varying thickness and pure levoglucosan were investigated (33) to study the effect of particle size on loss of levoglucosan by volatilization. It was observed that whereas the thin layer (0.36 mm) of cellulose permitted the easy loss of levoglucosan, an overlay of alumina or cellulose paper (0.9 mm) reduced the volatilization of levoglucosan.

During these studies the activation energy, measured by Arseneau (33), was found to be 36.8 K cal/mole for the dehydration reaction (250°C-320°C) and 45.4 K cal/mole for the depolymerization reactions (285-320°C).

Broido et al. in 1965 (28) demonstrated that the manner in which cellulose decomposes is modified by the presence of even low quantities of ash.

Kinetic studies on the thermal degradation of both wood and cellulose in the presence of air or steam have indicated that the process can be treated as simple first order (37). Halpern and Patai (29,31), in a series of papers which provide a useful survey of cellulose decomposition, have confirmed by differential thermal analysis-thermo-gravimetric analysis (DTA-TGA) techniques Broido's observations (28) that two types of reaction occur. The first is endothermic, near 360°C, and results mainly in tar formation - loss of levoglucosan from the cellulose. The second is exothermic and corresponds to formation of water, carbon oxides, and char.

Table 7. RESULTS OF DTA-TGA DETERMINATIONS PERFORMED SIMULTANEOUSLY ON α -CELLULOSE SAMPLES. (29)

Additive	D.T.A.			T.G.A.		
	Beginning of peak	Peak maximum	Peak area arbitrary units ± 2	Beginning of weight loss	Residue at 400°C	
10^{-4} mole/g	$^{\circ}\text{C} \pm 3^{\circ}\text{C}$	$^{\circ}\text{C} \pm 5^{\circ}\text{C}$		$^{\circ}\text{C} \pm 5^{\circ}\text{C}$	$\% \pm 2\%$	
None	310	380	-150	312	13	
NaHSO_4	280	350	- 75	280	16	
Na_2SO_4	260	390	- 76	290	21	
$0.1 \times \text{Na}_2\text{CO}_3$	330	387	- 23	290	16	
$0.2 \times \text{Na}_2\text{CO}_3$	330	382	- 19	283	20	
NaH_2PO_4	320	358	- 13	287	31	
NaOAc	343	370	- 10	260	23	
NaCl I	345	370	- 7			
II	375	385	+ 6	290	23	
Na_2CO_3 I	315	337	+ 5			
II	355	375	+ 5	240	27	
Borax	265	350	+ 55	280	43	

The effect of various additives on the decomposition rate of α -cellulose in vacuo is shown on Table 7. The amount of residue increases with additive basicity - endothermic reactions to produce tar predominate with no additive or with acidic additives.

Tikhomirova et al., (38) reported that the formation of oils from bark was due to the decomposition of phenols into hydrocarbons. Golova et al., (27), previous to Halpern and Patai, hypothesized that two types of reactions were present in the thermal decomposition of cellulose. Dehydration takes place due to the breaking of the C-O-C bond of the ring form of glucose, and decomposition occurs when the glucose molecules break apart at the site of the oxygen which links the molecules. Similar findings were reported in a paper by Kato (30). Schwender and Beck (39) listed the decomposition products of cellulose pyrolysis. These were levoglucosan, water, carbon dioxide, carbon monoxide, HCHO, MeCHO, aerolin, EtCHO, MeCOEt, MeOH, HCOOH, HOAc, n-PrCHO, Me₂CO, glyoxal, furfural, 5-hydroxymethylfurfural, lactic acid, valeraldehyde, ethylene glycol, glycolic acid, MeCOPr, and iso-PrCHO. Finally the products of glucose decomposition were stated by Walter and Fagerson (40) to be carbon dioxide, HCHO, furan, 2-methylfuran, diacetyl, AcOH, 2-propyl furan, furfural, 2-acetyl furan, 3-furaldehyde, 5-methyl-2-furaldehyde, 5-methyl-2-acetylfuran, 4-hydroxy-2-pentenoic acid, 1-(2-furyl)-1,2-propane-dione, 3-methyl-1,2-cyclopentane-dione, PhOH, and methyl-furoic acid.

CHEMICAL REACTIONS OF CELLULOSE TO PRODUCE FUEL

F. Fisher, Shrader, and Treibs (41) in 1921 pressure oxidized a sample of cellulose in a soda solution at 200°C and found that 42 per cent of the products were acids, mainly oxalic, formic, acetic and several

non-volatile acids. It was believed that the reaction was a combination oxidation-hydrolysis with sugars formed as intermediates. In a related study, Fisher and Shrader (42) reported that cellulose decomposed at 200°C at a rate that increased with increasing temperature. The products were gases, acids, and a solid residue. Lignin yielded carbon dioxide and a black coal-like substance. However, when heated in an alkaline solution to 300°C, cellulose completely decomposed to give carbon dioxide, an oil, and fatty acid. In still another paper (43) this same team found that when cellulose was heated to 400°C in a soda solution under pressure oxidation conditions, a gas, an oil, tars, and volatile fatty acids were formed. Under similar conditions, lignin was degraded to a gas, an oil, volatile acids, and benzoic and isophthalic acids.

Some other areas of early carbohydrate research were investigated by Willstatter and Kalb (44) who heated cotton samples to 250°C in the presence of hydroiodic acid and red phosphorus and noted that a solid and liquid hydrocarbon were present. In 1925 Fierz-David (45) and Fierz-David and Hanning (46) took samples of cellulose, heated them to temperatures between 450 and 470°C at pressures of 150 to 200 atmospheres in the presence of hydrogen and nickel hydroxide and recovered a tar, gases, and an aqueous distillate. Berl and Schmidt (47) heated cellulose in distilled water in a high pressure bomb to temperatures of 150 to 350°C. They reported evolution of carbon dioxide at lower temperatures and a gradual increase in methane production. An aqueous phase contained acetic acid and a brown amorphous product. In 1928 Frolich, Spaulding, and Bacon (48) found that wood under pressure produced methanol in a temperature range of 280 to 370°C. When they introduced hydrogen gas, methanol production increased. At a pressure of 200 atmospheres, with hydrogen gas

and nickel present, a cellulose sample was completely converted to gaseous and liquid products, which contained phenols and hydrocarbons. In 1925 Bowen, Shatwell, and Nash (49) claimed that when cotton samples were heated in hydrogen at a pressure of 40 atmospheres to a temperature of 420 to 440°C for several hours, a coke-like residue, water, carbon dioxide, light oils, and tars resulted. With the introduction of nickel oxide, a large amount of hydrogen was absorbed, with a corresponding increase in the amount of oil and tars produced.

In related studies reported in 1931, Lindblad (50) investigated the effectiveness of various catalysts on the destructive hydrogenation of wood. At temperatures of 250 to 400°C, cobalt sulfide, nickel sulfide, cupric hydroxide, molybdic acid, and zinc chloride all produced tars and oils from wood. Oil yields as high as 40 percent were reported. Routala (51) reported in 1930 that copper, iron and cobalt hydroxides, nickel formate, ammonium molybdate, and ammonium chromate gave oil yields up to 35 percent from sawdust. Berl and Biebesheimer (52) and Berl and Schmid (53) reacted cotton treated with sodium hydroxide and recovered gases and a tarry liquid. Temperature ranged between 310 and 330°C and the pressure varied from 180 to 220 atmospheres. The liquid was treated with hydrogen at 100 atmospheres at temperatures from 420 to 460°C for several hours. A hydrocarbon oil was recovered. Berl (54,55,56,57,58), in a series of articles, studied the conversion of cellulose in the form of sugar cane bagasse into substances which could be further hydrogenated to give useful petroleum products. He estimated in 1940 that if waste cellulose were converted by his process, approximately 10 percent of the nation's oil demand could be filled. Boomer, Argue, and Edwards (59) completely converted cotton and sawdust samples in tetralin to gases and

other products in 1935. Temperatures of 325 to 350°C and pressures of 180 to 275 atmospheres were used. Tetralin seems to possess a very active form of hydrogen, which can be used as a source of the mentioned gas as well as a reactant carrier. The products consisted of an oil, pitch, carbon dioxide, carbon monoxide, methane and olefins. Kalb and Strupp (60) found that tar oil, acetone, butanone, and methanol could be obtained by the destructive distillation of treated cellulose pulp wastes. Wallin (61) treated waste cellulose liquor, tar, phenol wood, straw, grass, leaves, peat, and brown coal with a solution of excess caustic alkali and heated these materials to 250°C under pressures from 40 to 500 atmospheres. Alcohols, aldehydes, acids, oils, ketones, and ammonia were recovered. Finally Henze and Wyatt (62) treated cellulose with a 7 percent solution of sodium hydroxide under a pressure of 5.4-6.1 atmospheres. This was then treated with hydrogen at a pressure of 325 to 380 atmospheres at a temperature of 250°C with Raney nickel present to give a colorless liquid, which contained acetic, propionic, butyric, lactic, and hydroxy-caprioic acids.

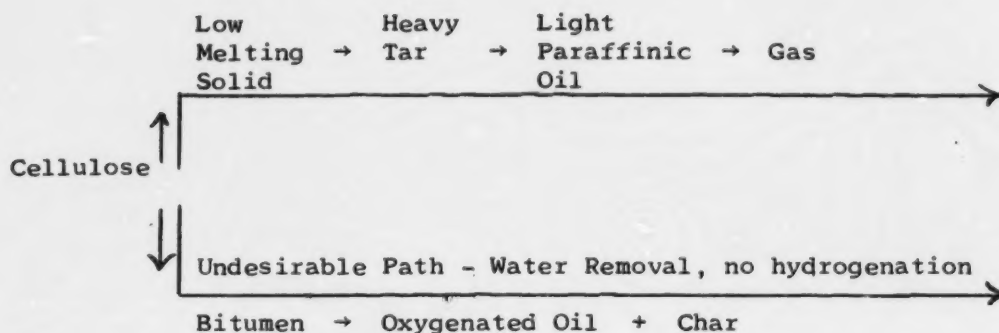
Heinemann (63) reported in 1950 that, when heated in an alkaline solution, cellulose reacted to give a bitumen, carbon oxides, water, methanol, phenols, and carboxylic acids. The bitumen was further reacted with hydrogen to give gasoline middle oils and lubricating oils. The gasoline was highly paraffinic in nature, with some aromatic and naphthenic compounds present. In a follow up article (64), sugar cane and bamboo sticks were again heated in sodium hydroxide to temperatures up to 454°C and, again, a bitumen formed. This was further hydrogenated to give a gasoline, naphtha, gas oil, lubricating oil, and an asphaltic residue.

More recent studies on cellulose and glucose chemistry by Gillet and Colson (65,66) showed that cellulose and sodium hydroxide react at temperatures between 150 and 350°C to give a coal-like substance and bitumens. These and other studies were aimed at developing theories about the formation of coal and petroleum from cellulose. Other recent studies (67) using iodine and hydrogen iodide as catalysts have found that cellulose produced an oil and a residue.

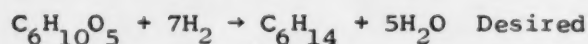
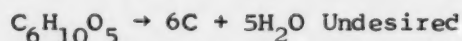
Henze (62) in his studies on catalytic hydrogenation of cotton found no hydrogenation below 250°C and postulated that high pressure hydrogenation involves two principal reactions:

1. The structure of cellulose collapses thermally at some weak links to produce unsaturated molecular fragments of reactive size. A liquid reaction medium acts as a solvent for the reactants and decomposition products and prevents the polymerization and condensation of the unsaturated intermediates.
2. These species are then stabilized by hydrogenation at high temperatures. Tropsch and co-workers (68) have suggested that catalyst primarily promotes the thermal decomposition reactions.

With an increase in the reaction temperature in the hydrogenation of cellulose, oxygen removal becomes more effective and hydrogen to carbon ratio is changed. This results in the change in the physical form of the products formed.



A simplified chemical scheme for the above paths was suggested by Weiss (26):



This is discussed in detail in the "WPI Process Concept" section.

Appell and co-workers (69) have provided some insight into the process of heating cellulose under H_2 and CO pressure in Na_2CO_3 solution. They suggest that, at low temperatures (250°C), an Aldol type of condensation takes place between carbohydrate rather than an oil. Hydrogen acts as a reducing agent and suppresses these condensation reactions by minimizing the carboxyl content of the reaction system. The yield of fuel oils from cellulose could also be increased by keeping the reaction medium more alkaline (thereby preventing the formation of organic acids).

Appell, Wender, and Miller have reported on their work at the Bureau of Mines (70,71,72,73,74). They made use of alkali carbonates and bicarbonates in aqueous medium under H_2 and CO pressure for converting organic wastes (animal waste, urban refuse, etc.) into fuel oils. Water was used as a reaction medium (vehicle) and also as a source of hydrogen, whereas carbon monoxide was the reactant gas to strip off oxygen from the cellulose molecule. They indicated also the possibility that active hydrogen

produced in-situ by the water-gas shift reaction was responsible for oxygen removal from cellulose. An autoclave with a rocking mechanism was used for batch studies and the temperature range was 250 -400°C. High pressures (102-272 atm.) were employed to keep water in the liquid phase (critical temperature of water is 375°C). Even though conversions of garbage and animal wastes were as high as 90%, the oils produced had a high oxygen content (10-20%), resulting in a low heating value.

Table 8 lists their results with cellulose charged to an autoclave containing water, pressured to 102 atm. with either carbon monoxide or hydrogen, and then heated for two hours at 350°C. Yields as high as 46 wt. % benzene soluble product were obtained.

Table 8. CONVERSION OF CELLULOSE TO OIL (71)

Cellulose	Gas	Catalyst	Conversion %	Benzene Soluble Product (wt. %)
Crude	CO		90	40
Ash Free	CO	None	63	17
Crude	H ₂		60	20
Ash Free	CO		94	46
Ash Free	H ₂	Na ₂ CO ₃	90	27

They also extended their work to municipal refuse, newsprint, and sewage sludge and developed a low temperature version of the process operable at 250°C. Table 9 shows products obtained from municipal refuse.

Table 9. CONVERSION OF MUNICIPAL REFUSE TO OIL^a
(wt. %)

Gas	CO	H ₂
Conversion	94	80
Product distribution		
Oil ^b	41	18
Residue	6	20
Water	27-36	45
CO ₂	15-24	15
Other	2	2

^a20 min. at 380°C, 102 atm initial pressure

^bComposition: C, 79.6%; H, 9.5%; N, 1.9%; S, 0.13%

The oils had large amounts of oxygen present, chiefly as carboxyl and carbonyl compounds. When the reaction temperature reached 380°C, it was believed that a water-gas shift reaction took place, which formed hydrogen and probably hydrogenated some of the compounds present. In a related study (75), oil conversions up to 85 percent were reported. These oils contained large amounts of oxygen and nitrogen compounds, but very little sulfur. Oxygen was in the form of carboxyl, ketones and phenols. Another paper (76) stated that pyrolysis of solid waste materials gave a solid residue, tar, light oils, hydrogen, methane and ethylene. Analysis indicated olefinic and aromatic substances were present and the light oils contained benzene and toluene. Temperatures between 750°C and 900°C were investigated.

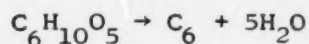
Corey (77) provides a summary of pyrolysis, hydrogenation, and incineration work currently proceeding at the Bureau of Mines on municipal refuse and estimates that a ton of dry refuse can yield approximately 2.4 barrels of oil.

The main thrust of U.S.B.M. studies has been the conversion of agricultural wastes to fuels. The annual production of agricultural wastes (600 million tons) (74) is about three times that of municipal refuse (220 million tons) (10).

In summary, one approach to the solid waste disposal problem that was experimentally shown to be feasible as early as 1925 is to liquefy wastes to useful products, such as oil. The most recent confirmation of this possibility was by researchers at the Bureau of Mines Coal Research Center (Bruceton, Pa.) who successfully processed cellulose and produced a significant oil fraction.

THE WPI PROCESS CONCEPT

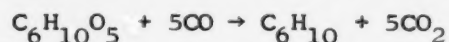
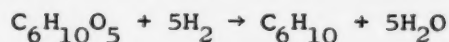
Consider the process of heating a carbohydrate. It first passes through a caramelized state and ultimately is converted to carbon. (For example, charcoal made by heating wood.) The pyrolysis reaction can be written as



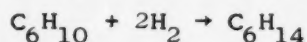
using glucose as a model compound. This is an undesirable reaction from the standpoint of producing liquid hydrocarbons. Crude oil is higher-valued, the higher its hydrogen content*, e.g., paraffinic vs. naphthenic crudes. In fact, the availability of hydrogen in refineries has led to processes such as hydrotreating, hydroforming, and hydrocracking especially designed to add hydrogen to oil. As an example, an intrinsic part of the Shell process to convert 7° API Athabasca tar to 33° API sweet crude oil requires extensive hydrotreating facilities (78).

*In refinery jargon, the "lighter" the crude, the higher the API gravity (the lower the specific gravity), the more useful is the oil.

The only way for a liquid product to be formed from cellulose is for oxygen, rather than water, to be stripped from the molecules. This is evidently what occurred to some extent in work using either or both hydrogen and carbon monoxide in the absence of a metallic hydrogenation catalyst.

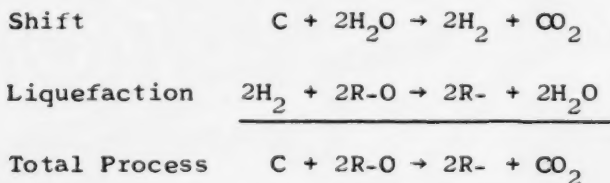


The stoichiometry of the above equations is idealized and an oversimplification of the facts. Concerning the actual chemical structure of the compounds labelled C_6H_{10} , we shall not speculate at this time. Certainly there is no question that the C_6H_{10} can be upgraded by hydrogenation.



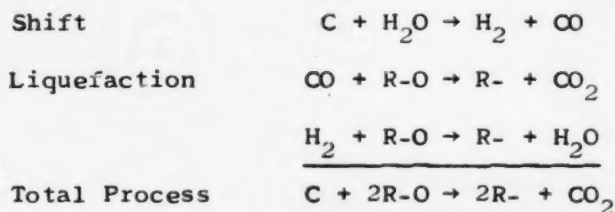
Also, oxygenated compounds may undoubtedly form (e.g., phenols, cresols).

It must be realized that, unless a source of hydrogen such as reformer hydrogen is available, it must be provided by the water gas shift reactions, which use carbon and a hydrocarbon as raw materials. The reaction of liquefaction will then be removal of oxygen from an oxygenated compound. The overall process is then the sum of the two reactions, such as indicated below, where R-O represents an oxygenated species. Note that, so far as raw materials are concerned, neither hydrogen nor water appears as a reactant or product of the overall process, even though both are central to the individual steps.



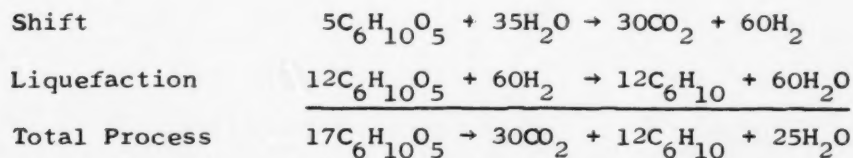
If the synthesis gas ($\text{CO} + \text{H}_2$) rather than hydrogen is obtained from

the shift reaction and used as reactant, the same overall reaction results as above.



However, this sequence requires that carbon monoxide be an actual reactant. Whether this is so or not is not conclusively known at present. If not, it may be that the water gas reaction proceeds in-situ during liquefaction, but this might be at less than the optimal shift conditions and, if so, not preferable to hydrogenation alone.

If the carbon source for the shift reaction is cellulose, then the following set applies



The overall reaction will be the same, no matter whether the reaction gas is hydrogen or synthesis gas.

Since a self-contained process will use cellulose as the source of synthesis gas or hydrogen, it is interesting to note the theoretical yield of oil:

$$\frac{12}{17} \times \frac{82}{162} = 35.7 \text{ wt. \%}$$

If the C_6H_{10} has specific gravity of unity, this amounts to 2 Bbl/ton. Cyclohexene which is C_6H_{10} , but obviously far structurally from the product that would be projected from cellulose liquefaction, has a specific gravity of 0.810. If the oil produced were this light, it would have a yield of 2.47 Bbl/ton.

Apparently, water plays a role in the intermediate steps of the liquefaction reaction. In all probability, steam will be present in an ultimate process. However, there must be a carrier liquid phase and, if this is water, there is a limitation not only to operation below its critical temperature, but also a requirement of severe pressures at elevated temperatures to maintain the liquid state. It should also be noted that oils high in oxygen content are not particularly desirable fuel; and oxygen content as well as carbon-hydrogen ratio is required to establish the quality of oils produced.

In the WPI Process, oil rather than water, is used as the carrier medium transporting the slurry of dried, ground solid waste and catalyst to the continuous stirred tank reactor. There, at a hydrogen pressure of 70 atmospheres and a temperature of 450°C, the carbohydrates are converted to hydrocarbons. The products are forced from the reactor and cooled before separation into gas and liquid-solid streams. A portion of the product oil is recycled to be used as the carrier medium. This process is represented schematically in Figure 5.

CELLULOSE PROCESSING SYSTEM

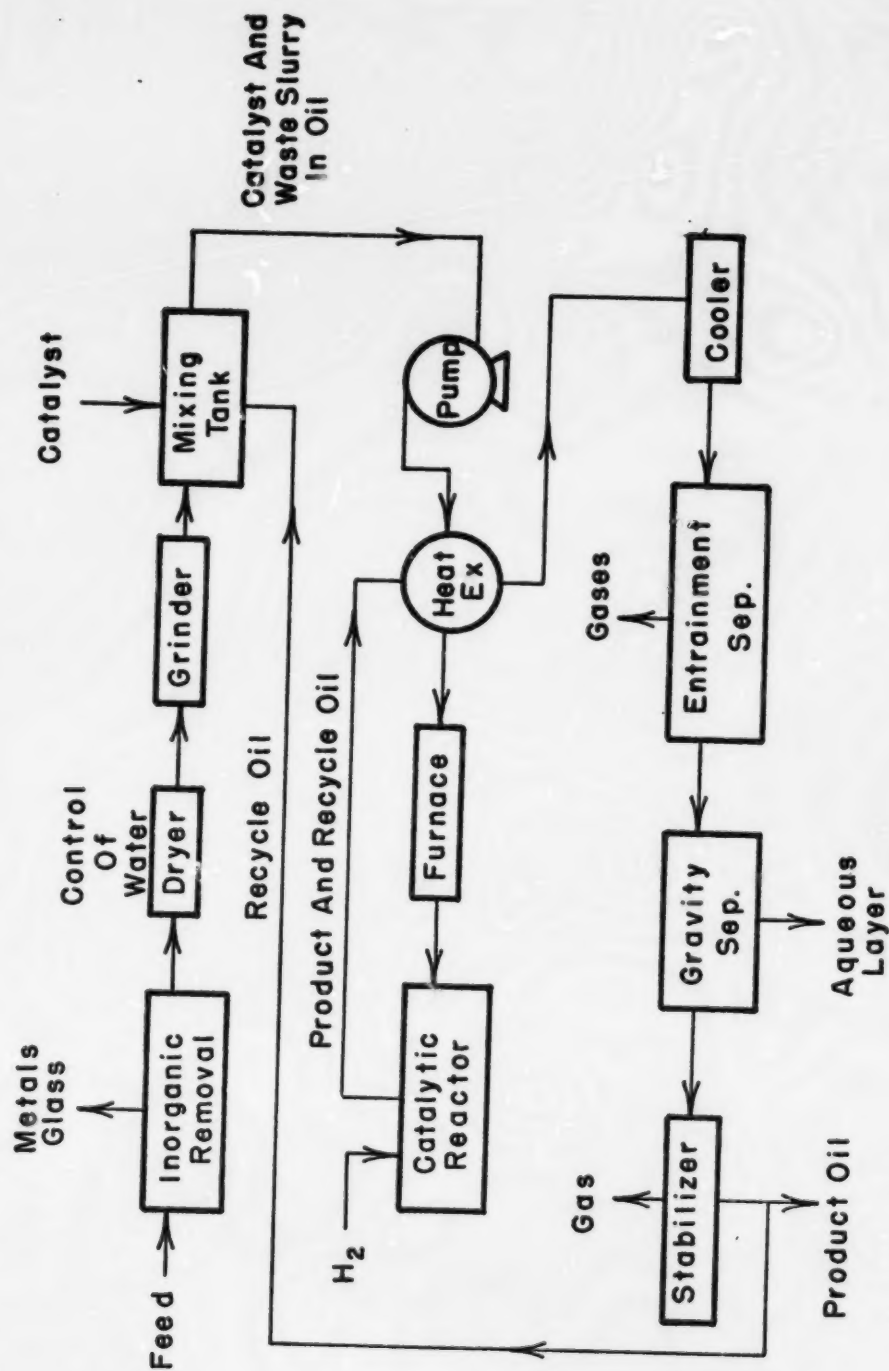


Figure 5

FACILITIES

INTRODUCTION

The Resource Recovery Laboratory for Solid Waste Liquefaction is located on the ground floor of Goddard Hall. The layout of this facility is shown in Figure 6. There are three functional areas: 1) the main laboratory; 2) the control room; and 3) the barricade room.

The main laboratory houses most of the major pieces of analytical instrumentation, the wet analysis section, and the office equipment (desks, chairs, file cabinets). Both the control room (containing the control consoles, dedicated chromatographs, and on-line infrared analyzers) and the barricade room (housing the CSTR unit, the gas storage cylinders, and the rocking 300 cc Aminco Autoclave) are high ventilation areas. Air in them is replaced every 1.1 minutes to reduce hazards from the build up of explosive or noxious gases. The barricade room has reinforced walls (6" concrete block, 1" plywood, and 20 gauge steel) and pressure relief ceiling.

PROCESSING EQUIPMENT

The Solid Waste Processing System consists of a continuous stirred tank reactor (CSTR); solid, liquid, and gas feed sections; a product withdrawal system; and a dedicated product gas analysis train. The total system is represented schematically in Figure 7.

The dry solid waste, free of glass and metal, is ground using an Alpine American Model 25A Hammer Mill and then pulverized in 8 liter Lumard ball mills. (Presently, newspaper is used as a model reactant.) The powdered solid waste is then slurried with carrier oil (mineral oil) in a 75.7 liter stainless steel steam heated mixing tank. The slurry is pumped into the CSTR by a Milroyal Model A piston-action, constant volume

Resource Recovery Laboratory

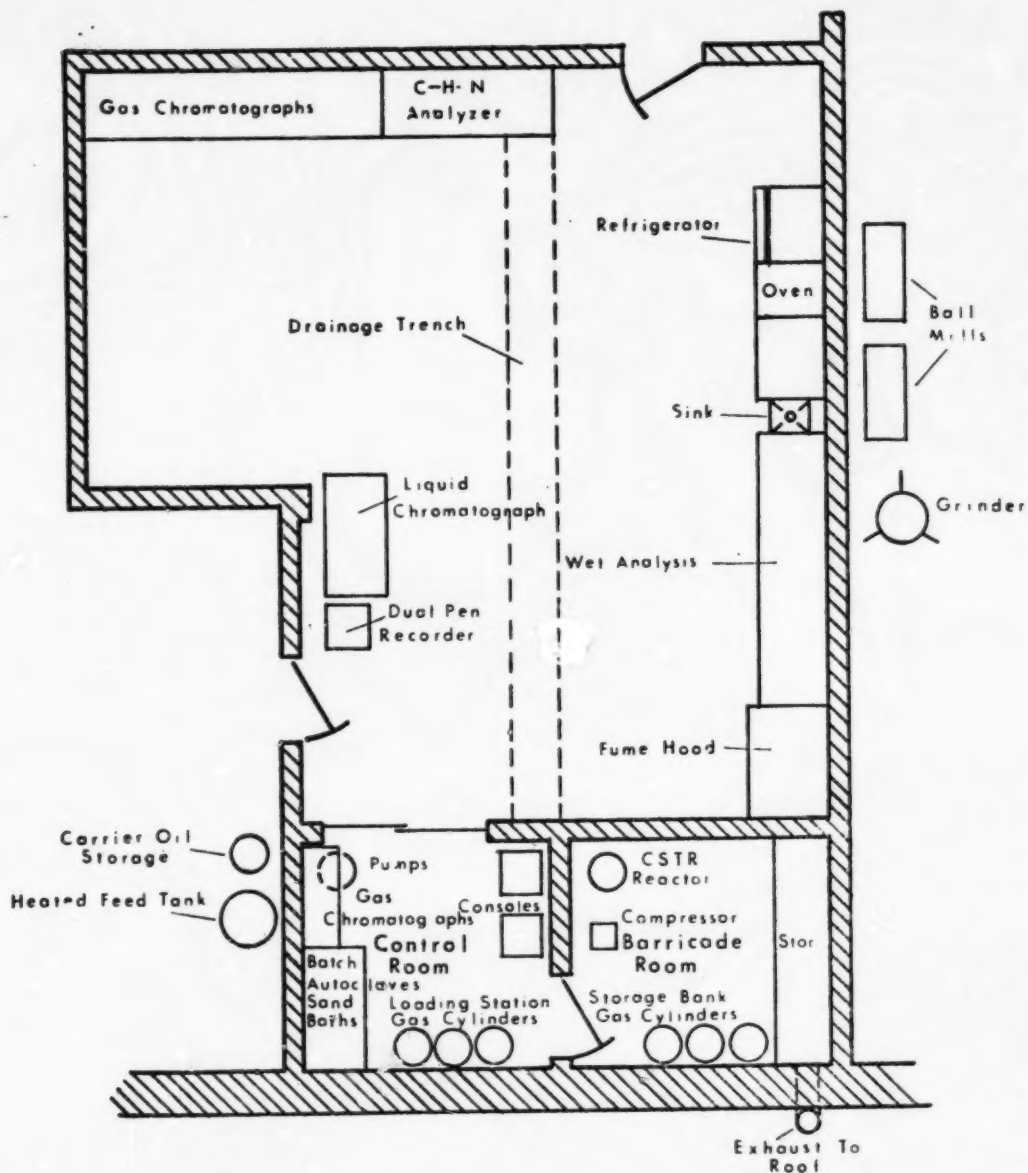


Figure 6

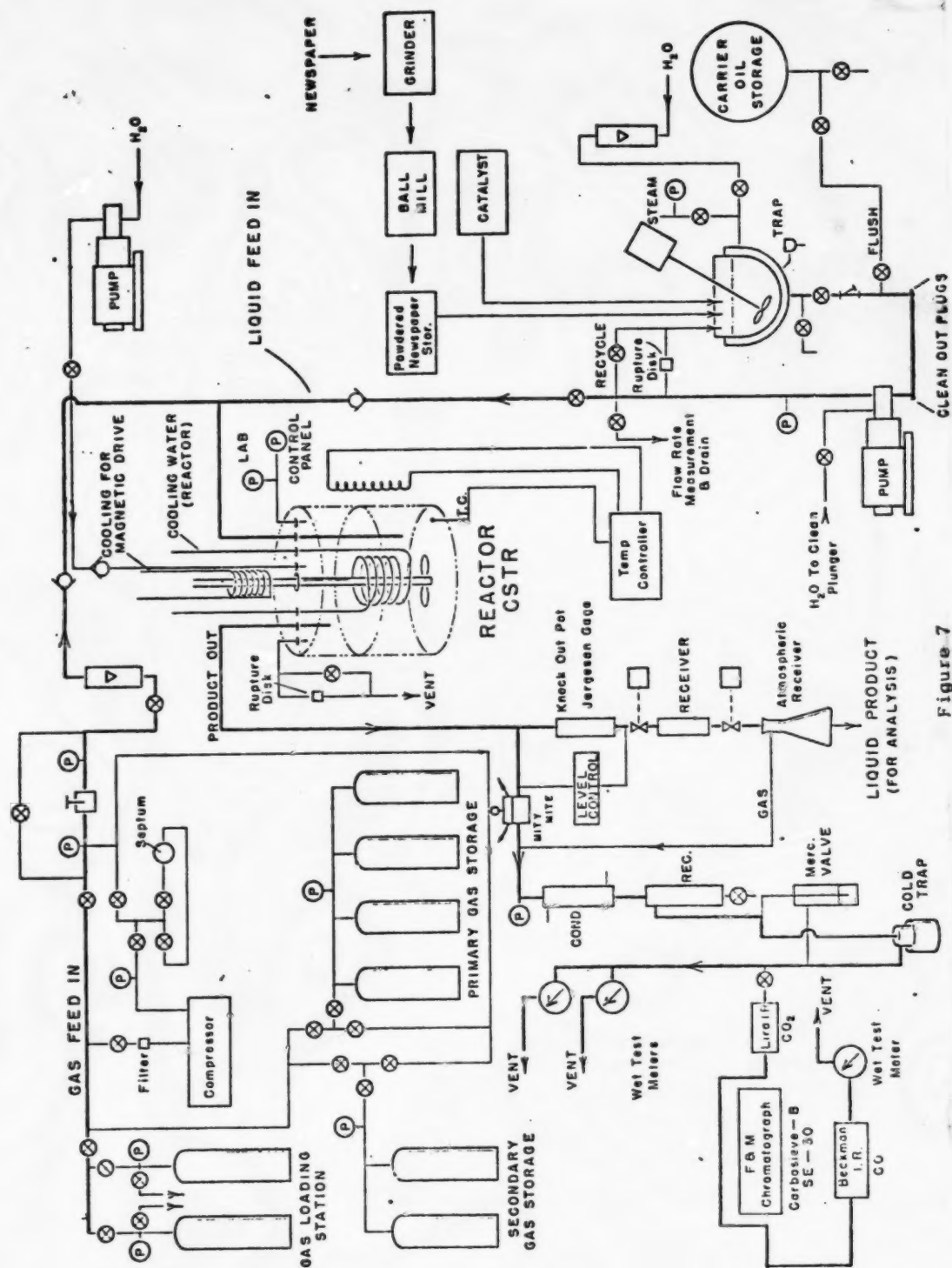


Figure 7

pump (maximum capacity: 12.5 liter gal/hr; 300 atm.). A Lapp Pulsafeeder Pump (Model LS-30) is used to pump water separately at a controlled rate into the reactor. All liquid-feed lines are heated and insulated both to prevent plugging and to preheat the feed. Make-up gases to the storage banks are loaded from the control room into the storage cylinders in the barricade room through a gas compressor located in the barricade room.

The CSTR is a 1-liter stainless-steel autoclave manufactured by Autoclave Engineers, Inc., Model AFP-1005. This vessel is equipped with a magne drive stirrer, thermowell, heater, cooling coils, baffles, liquid and gas inlet ports, a product withdrawal line, and a rupture disc (340 atm) to prevent explosion. The takeoff volume is presently set at 720 ml. The reactor temperature is regulated by a Honeywell temperature controller. An internal cooling coil permits rapid quenching of the autoclave.

The gaseous and liquid products are cooled and then separated in a Jerguson knock-out pot. The liquid products are drained automatically by a liquid-level controller and valve system to an atmospheric receiver where samples are withdrawn for analysis.

The line from the Jerguson Gage to the Grove 91-W Mity-Mite back pressure regulator is traced with a 0.318 cm copper cooling coil to condense volatiles and to protect the regulator's diaphragm, which must remain under 100°C. High pressure product gases pass through the Mity-Mite which permits the reactant gas flow to be controlled by a needle valve ahead of the inlet gas rotameter. The product gases are again cooled to condense volatiles and then divided into two streams. Ninety percent of the gas is vented through two wet test meters. Ten percent of the gas is passed through a dedicated analysis train where carbon

monoxide and carbon dioxide are monitored by Lira and Beckman Infrared analyzers, respectively. Hydrogen and light gases are measured by gas chromatography (see Figure 8).

A high pressure trickle bed reactor was constructed for post-treatment of the fraction oil. Hydrotreating as well as reactions with carbon monoxide and water can be conducted in the system shown in Figure 9. In a trickle bed reactor, the feed drips over the catalyst bed, wetting it but not flooding it. This effects excellent solid to liquid and liquid to gas contact. Both gas and liquid slurry feeds are preheated before entering the heated (to 434°C) reactor with its 5-10 cc catalyst zone. Pressures (to 136 atm) are controlled by a Mity-Mite back pressure regulator through which all products pass on their way to an atmospheric separator. Analysis of products is performed off-line.

ANALYTICAL EQUIPMENT

Off-line major analytical instrumentation includes: 1) a CHN analyzer with Cahn Gram Electrobalance for elemental analysis of liquid and solid products; 2) a Waters ALC 201 High Pressure Liquid Chromatograph with RI and UV detectors and dual pen recorder for hydrocarbon type analysis (PONA) of liquid products and for separation, isolation, and identification of liquid and solid products; 3) temperature programmable FID and TC gas chromatographs for simulated true boiling point analysis of oils; 4) a duPont Model 990 DTA console and high pressure DSC cell for microscale reaction studies and catalyst screening; 5) a high temperature furnace for proximate analysis of solids; 6) an interfaced Perkin Elmer 900 Dual FID Gas Chromatograph interfaced to a duPont 21-491 mass spectrometer for product separation and identification; and 7) a Parr Model 13051 Oxygen

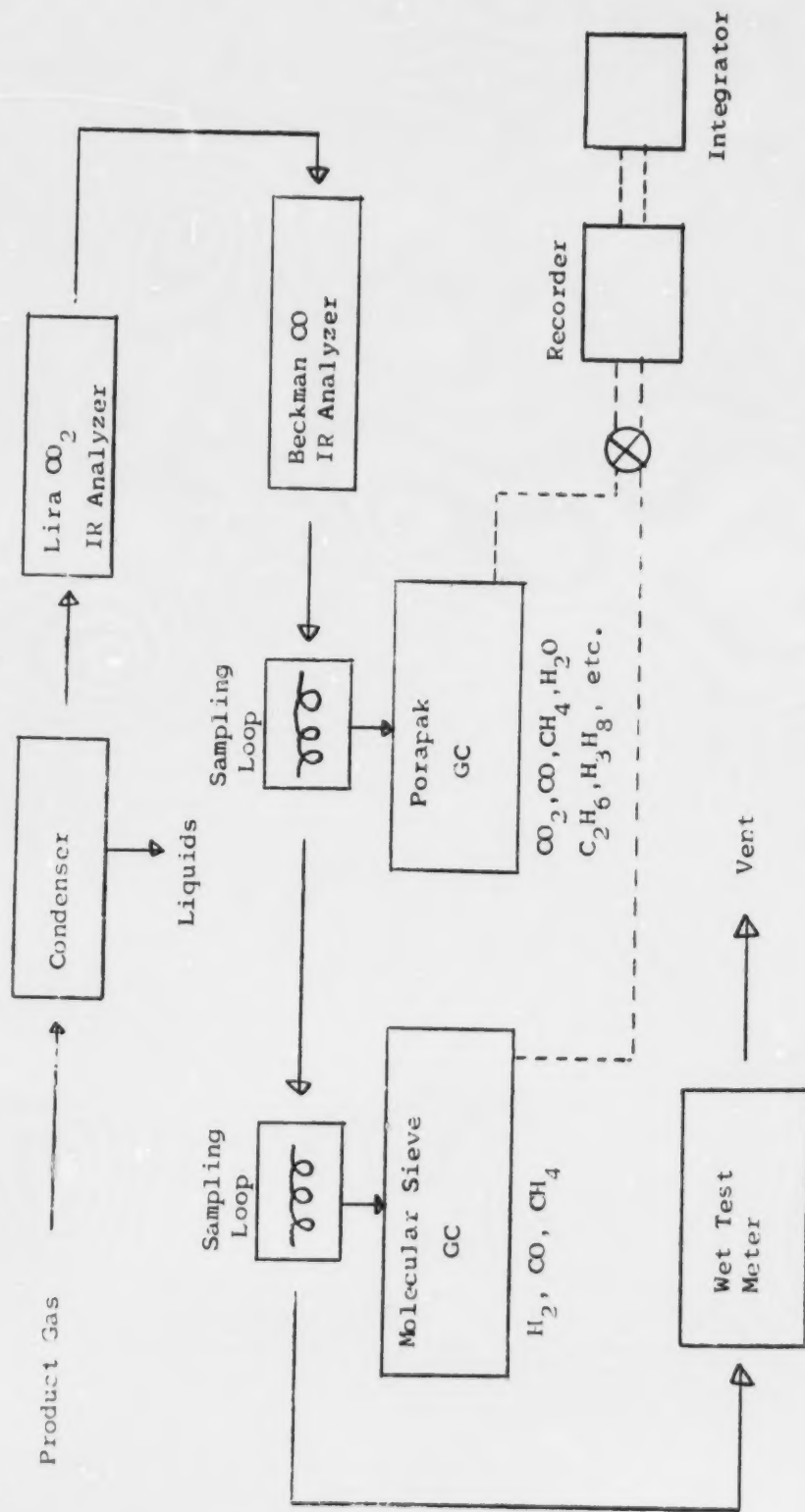


Figure 8: Gas Analysis System

HIGH PRESSURE TRICKLE BED REACTOR

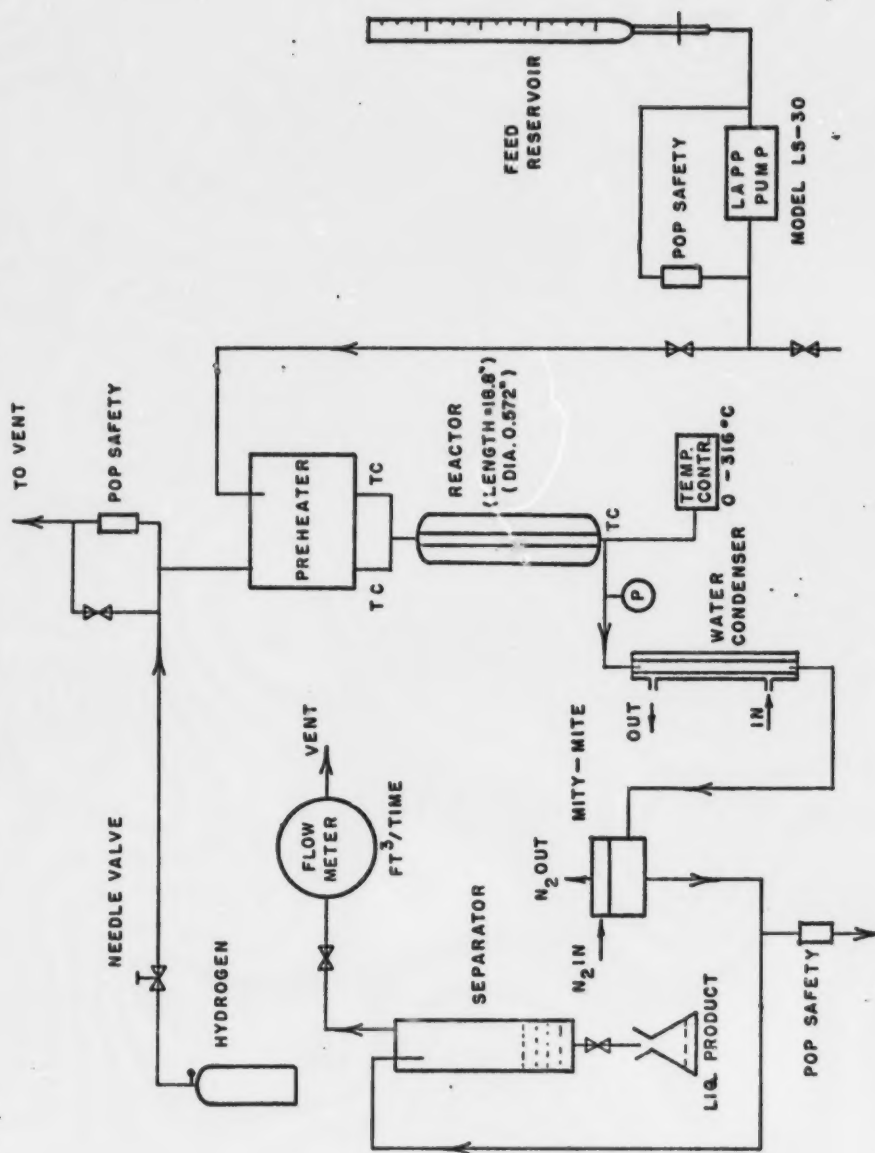


Figure 9

Bomb Calorimeter for determination of heating values. Also available are infrared and ultraviolet-visible spectrometers for product identification.

COMPUTATION OF COMPLEX EQUILIBRIA

SUMMARY

Equilibrium product distribution was computed for the cellulose liquefaction process in order to obtain information on the effects of reaction parameters (temperature, pressure, and reactant phase compositions). Computation (RCA spectra 70/46) was done in the temperature range of 600 -1000°K and pressure range of 50-100 atm. Cellulose was taken as $C_6H_{10}O_5$ and various initial compositions of the reactant gases, e.g., H_2 , CO and H_2O , were used to study the product compositions at equilibrium. A computer program devised by Ma and Shipman (79) of W.P.I. was used for these calculations.

The equilibrium calculations indicate that hydrogen rather than carbon monoxide is the preferred reactant gas - at least from an equilibrium point of view. To completely suppress char formation (an undesirable product), a high partial pressure of hydrogen or water is advantageous. When CO is used for oxygen stripping, char or carbon will always be present at equilibrium. Higher temperatures also suppress coke formation and increase hydrogen composition in the product gas. The yield of liquid hydrocarbons decreases with increasing temperature. Consequently, there will be an optimum temperature to eliminate coking but simultaneously increasing the yield of liquid hydrocarbons.

METHOD

For a given pressure, temperature, amount of each chemical element, and the chemical potentials of all possible species at a reference pressure (1 atm.), the equilibrium composition was calculated. On the basis of a preliminary estimate of the composition, the program then computed the amounts of the various species. These were obtained by direct Gibbs

function minimization (using a modified Naphthali method). This estimate was used to obtain an exact solution by application of the Newton-Raphson method to the non-linear set of equations describing the equilibrium conditions.

The species chosen to be present were: carbon monoxide, hydrogen, carbon dioxide, methane, water, oxygen, ethane, n-pentane, n-hexane, cyclohexane, cyclohexene, ethylene, 1-pentene, 1-hexene, acetylene, benzene, and unreacted carbon. All species except carbon are gas phase. The number of phases considered was two.

The tolerance permitted for rejecting a particular species has an appreciable effect on the computer time needed. A judgment on the part of the user was needed to establish the optimum tolerance allowed. In our calculations, it was established that for temperatures 800°K and 1000°K a tolerance of 10^{-4} required about 20 to 50 seconds of computer time for each set of data. For temperatures below 800°K the time required increased to 10 minutes. At these temperatures, a tolerance of 10^{-2} was used. At this value, only 15 to 30 seconds of computer time were required. The total number of independent reactions possible in our case is 14. The elements considered were 3 (C, H and O).

It was found that only the following species were present in significant quantities in the product mixture at equilibrium: carbon monoxide, carbon dioxide, hydrogen, water, methane, ethane, and unreacted carbon.

Effects of the following parameters were studied:

1. Reaction temperature (Figure 10) 600°K, 800°K, 1000°K
2. Reaction Pressure (Figure 11) 50 atm., 75 atm., 1000 atm.
3. Initial reactant composition (cellulose is considered as $6C + 5H_2O$)

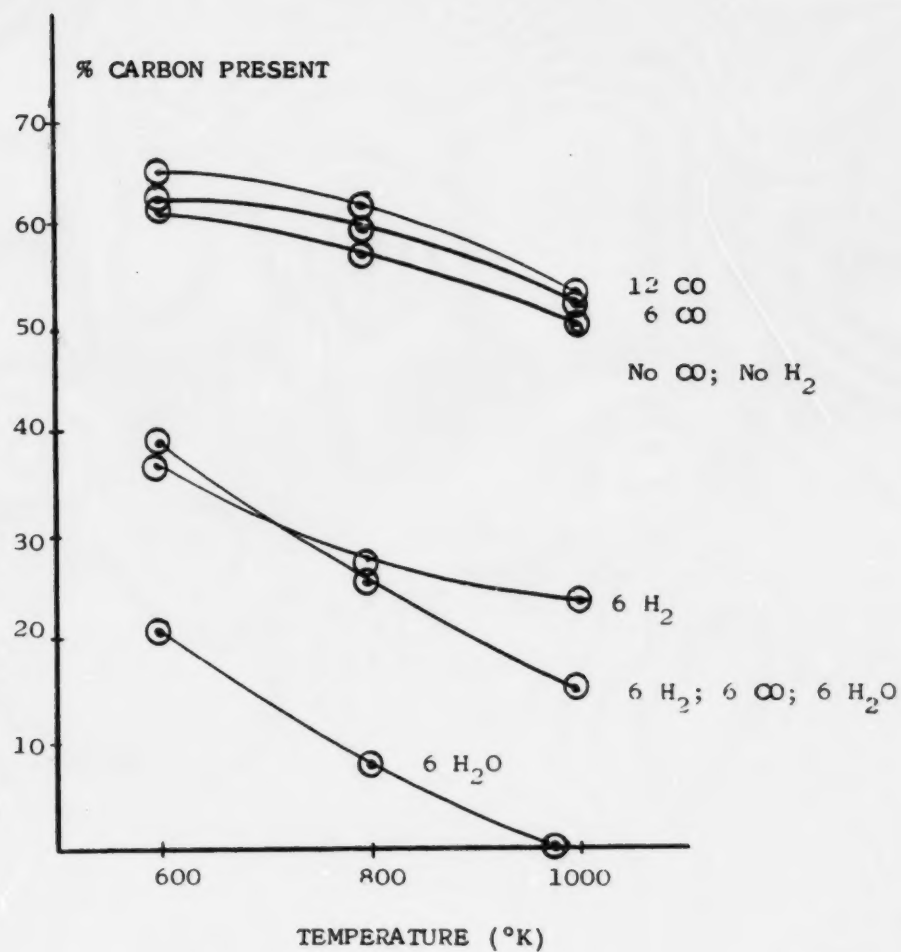


Figure 10: Effect of Temperature and Initial Composition on Coking;
 $P = 50 \text{ Atm.}; 1 \text{ mole of cellulose equivalent}$
 $(6C + 5H_2O)$

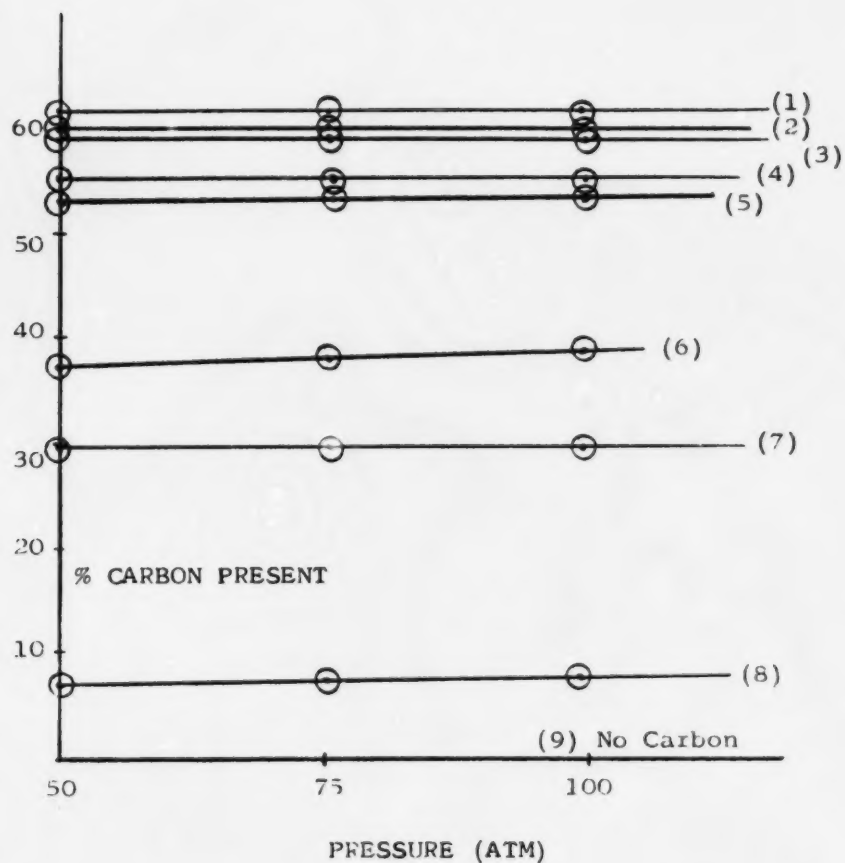


Figure 11: Effect of Pressure and Initial Gas

Composition on Coking; $T = 800^{\circ}\text{K}$;

1 mole of cellulose equivalent ($6\text{C} + 5\text{H}_2\text{O}$)

(1) 12CO ; (2) 6CO ; (3) No H_2 or CO ; (4) 6CO and 6H_2 ;

(5) 12CO and 12H_2 ; (6) 6H_2 ; (7) 6CO , 6H_2 and $6\text{H}_2\text{O}$;

(8) $6\text{H}_2\text{O}$; (9) $12\text{H}_2\text{O}$ or 12H_2 or 6H_2 and $6\text{H}_2\text{O}$ or

6H_2 and $12\text{H}_2\text{O}$ or 12H_2 and $12\text{H}_2\text{O}$

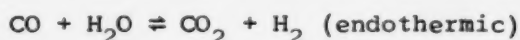
EFFECT OF REACTION TEMPERATURE

Keeping other parameters fixed, the effect of temperature in general can be seen from Figure 12, as an example:

As temperature increases, the percentage in product gases:

1. of CO formed increases
2. of CO₂ increases
3. of H₂ increases
4. of H₂O decreases
5. of CH₄ (or hydrocarbons) decreases

So far as hydrocarbon (viz., CH₄) formation is concerned, increasing temperature is not advantageous. The water-gas shift equilibrium



is favored to proceed to the right at high temperatures. Temperature was found to have similar effects on equilibrium gas composition at other pressures and different gas compositions.

The effect of temperature on suppression of carbon formation in the system (for no coking) is shown in Figure 10 for different initial gas compositions with 1 mole of cellulose. It would be advantageous to use higher temperature for suppressing carbon deposition.

Consequently, with respect to equilibrium, there will be an optimum temperature to eliminate coking and simultaneously maximize yields of hydrocarbons.

EFFECT OF PRESSURE

As demonstrated by Figures 13 and 14 pressure does not have a significant effect on the product gas composition. From the general trend of the curves on Figures 13 and 14 we can conclude that with increased pressure

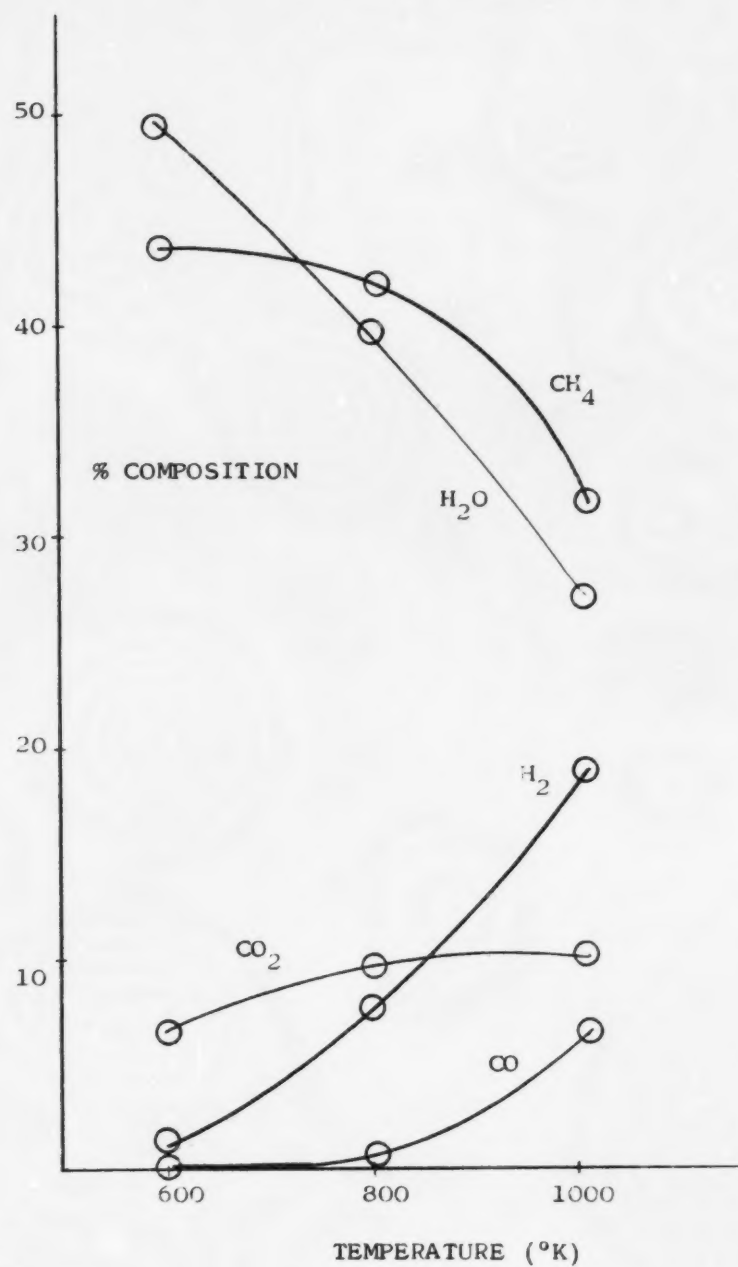


Figure 12: Equilibrium Composition of Gases;

$P = 50 \text{ Atm.}; 1 \text{ mole of cellulose equivalent}$
 $(6C + 5H_2O)$
 and 6 moles of hydrogen

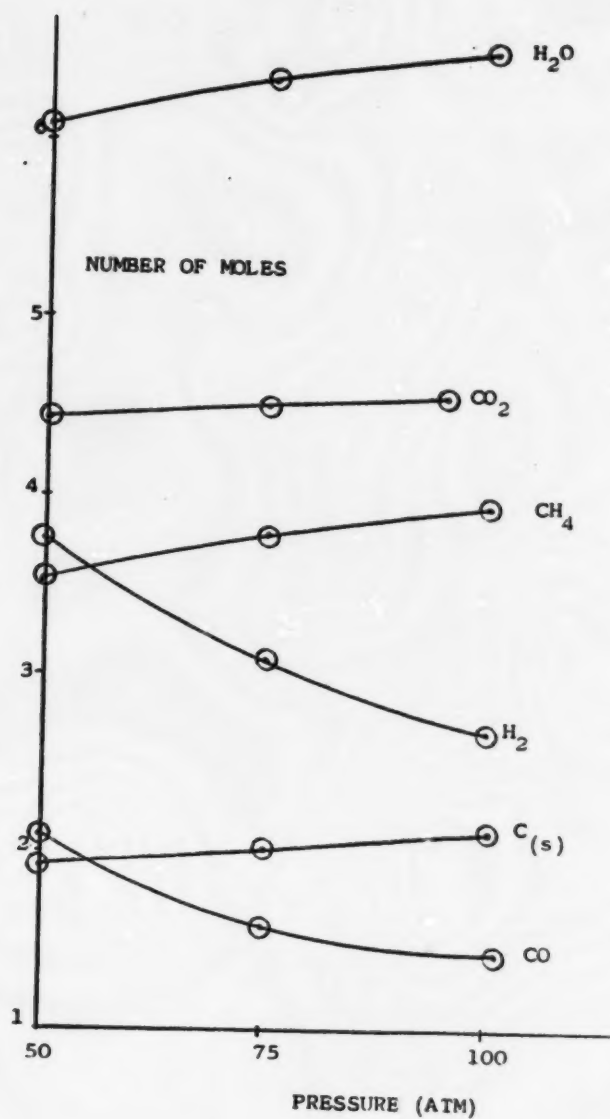


Figure 13: Effect of Pressure on Equilibrium

Composition: $T = 1000^\circ\text{K}$;

1 mole of cellulose equivalent ($6\text{C} + 5\text{H}_2\text{O}$)

6 moles of carbon monoxide and 6 moles of water.

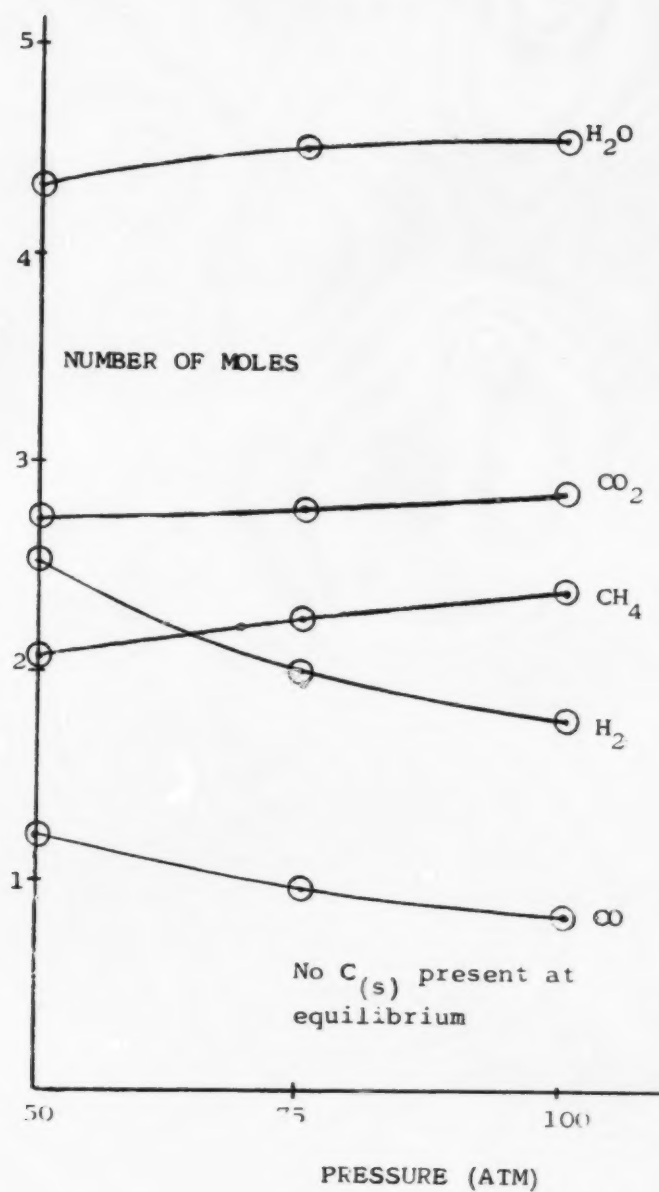


Figure 14: Effect of Pressure on Equilibrium Composition; $T = 1000^\circ\text{K}$; 1 mole of cellulose equivalent ($6\text{C} + 5\text{H}_2\text{O}$) and 6 moles of water

1. H_2 decreases
2. CO decreases
3. Hydrocarbons, CO_2 and H_2O increase.

EFFECT OF HYDROGEN

Comparing Figures 12, 15 and 16 we reach the conclusion that as the amount of hydrogen per mole of cellulose is increased

1. H_2O decreases
2. H_2 increases
3. CO_2 decreases
4. CH_4 increases
5. CO decreases.

This shows that increasing the amount of initial hydrogen is favorable so far as product gas composition is concerned.

Figure 10 shows that the amount of carbon formed in the system decreases rapidly as the amount of H_2 is increased. At $H_2/\text{cellulose} = 12$ all the carbon in the system has reacted (abscissa). Hence so far as coke deposition in a practical process is concerned it would be desirable to use a $H_2/\text{cellulose}$ ratio that will preclude a thermodynamic requirement for elemental carbon.

EFFECT OF CARBON MONOXIDE

Comparing Figures 12 and 17 it is seen that as the ratio of CO/cellulose is increased the amounts of

1. CO_2 increases
2. water decreases
3. H_2 decreases
4. hydrocarbons decrease in low temperature range
5. CO increases slightly.

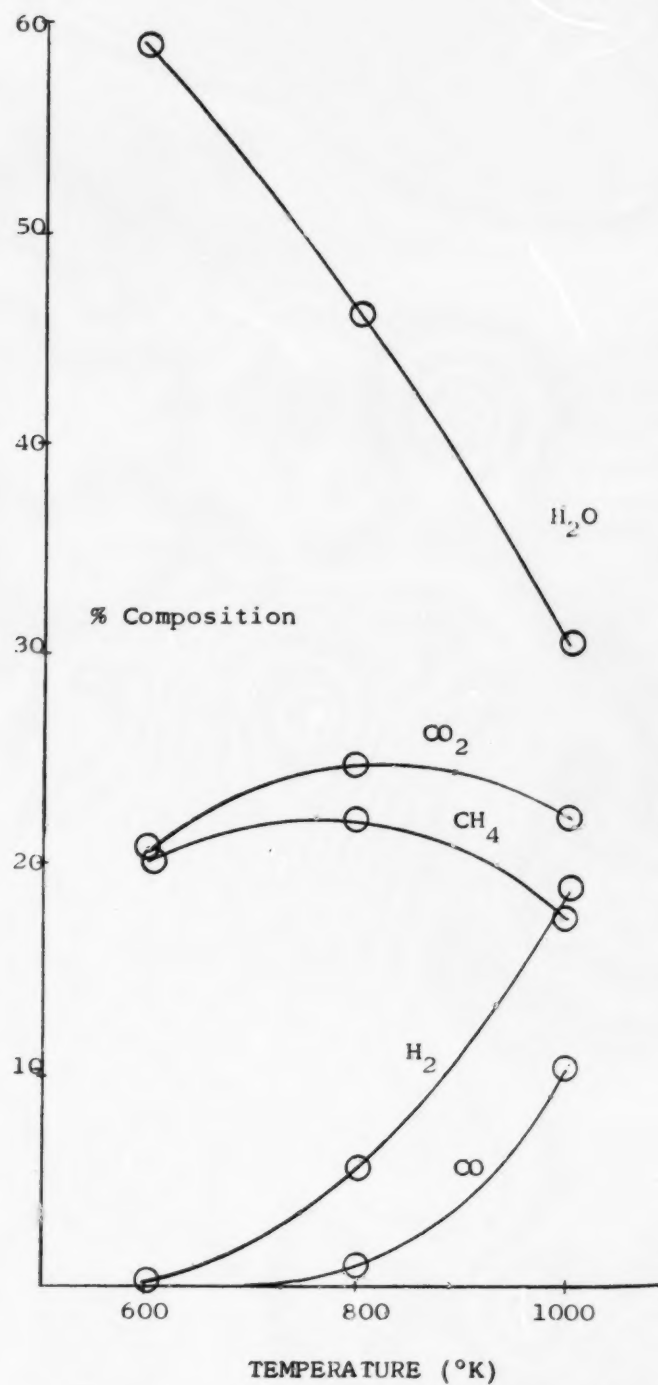


Figure 15: Equilibrium Composition of Gases;
 P = 50 Atm.; 1 mole of cellulose
 equivalent (6C + 5H₂O)

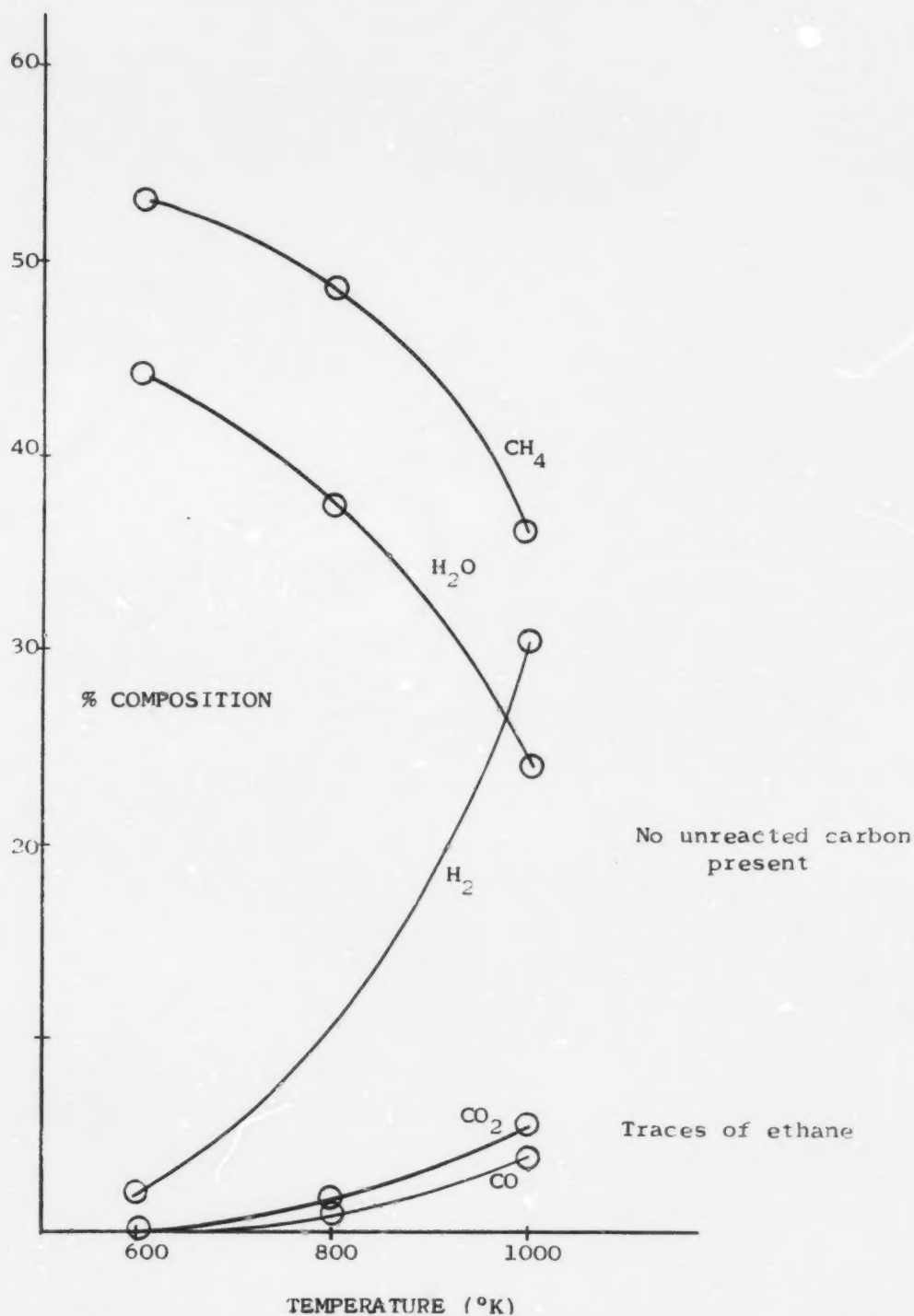


Figure 16: Equilibrium Composition of Gases;

P = 50 Atm.; 1 mole of cellulose equivalent ($6C + 5H_2O$)
and 12 moles of Hydrogen

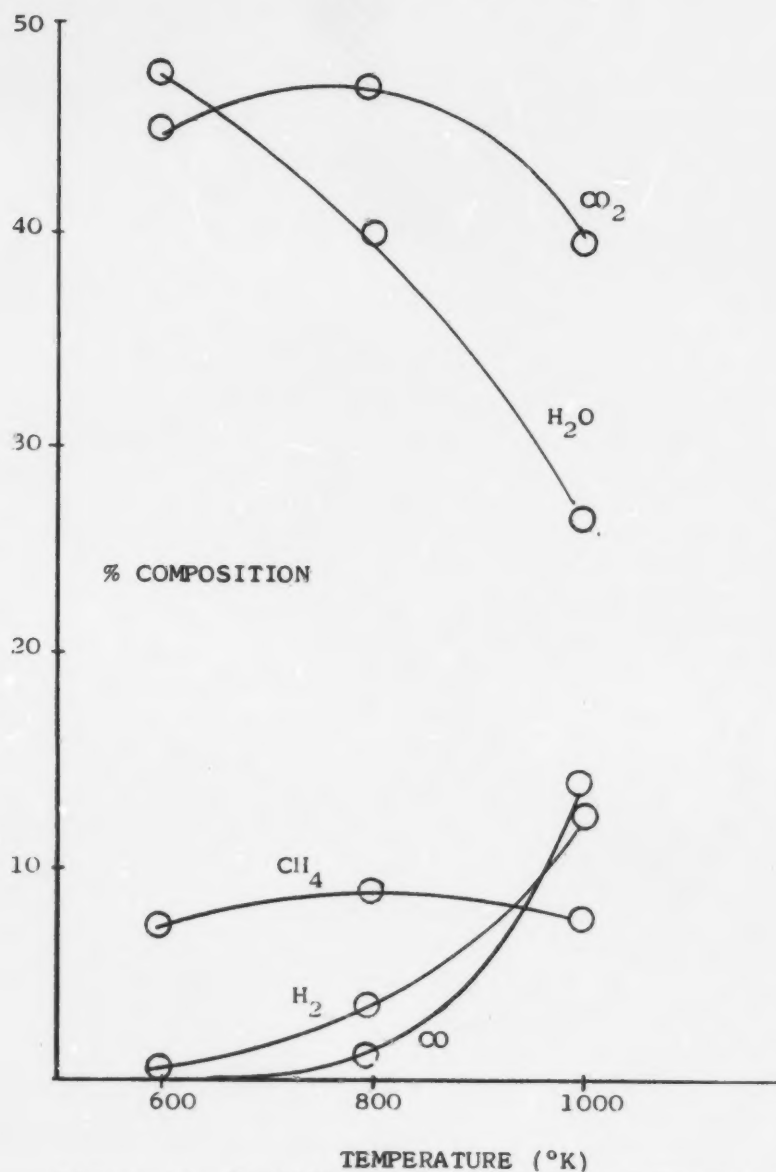
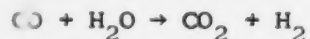


Figure 17: Equilibrium Composition of Gases;

$P = 50 \text{ Atm.}$; 1 mole of cellulose equivalent
 $(6\text{C} + 5\text{H}_2\text{O})$ and 6 moles of carbon monoxide.

This could be interpreted as follows:



The shift reaction is going towards the right and CO_2 is formed at the expense of CO . Figure 10 shows that there is more coke deposition as the amount of CO initially present in the system is increased. Hence, the presence of CO in the initial mixture is not desirable, according to the equilibrium calculation.

EFFECT OF WATER

From Figure 10 we can see that the presence of water in the system (initially) is very desirable so far as suppression of carbon formation is concerned. At a H_2O /cellulose ratio of 6 in the high temperature range all the carbon has reacted. As the amount of water is increased there is no carbon left even at low temperatures.

The effects of various combinations of CO , H_2 and H_2O on coking with temperature are shown in Figure 10. CO enhances coking. Figure 11 shows that pressure, per se, has negligible effect on coking. H_2O and H_2 suppress coking, CO should be avoided in large quantities.

PRELIMINARY EXPERIMENTATION ON POWDERED NEWSPAPER

GRINDING NEWSPAPER

Newspaper was cut into 1" wide strips and fed into the hopper of an Alpine Hammer Mill Grinder, Model 25A, equipped with an 0.5 mm screen. The desired particle size for slurry pumping is 80% passing through a 200 mesh screen or 100% passing through an 80 mesh screen. Since the Hammer mill did not achieve this size reduction the product from the grinder had to be ball milled. 3 ball mills are being used continuously for reducing the particle size of the product from the hammer mill. Specifications of the ball mills used are given in Table 10.

Table 10. SPECIFICATIONS OF BALL MILLS

Cylinder

Porcelain jar
Diameter 8.75"
Height 8.50"
Contents 1.25 gallons

Balls

High density porcelain cylinders
13/16" x 13/16" -- 18 to a lb.
Number used = 180

Product Capacity

200 gms in one charge

Ball mill rpm = 60

Since the capacity of the ball mills is limiting, newspaper was passed through the Hammer Mill Grinder several times before it was fed to the ball mill. A modest study of total time required for grinding and ball milling was made. Samples were taken from the grinder for different number of passes. For each of these samples the time required by the ball mills to produce the desired particle size was determined by feeling the powder.

Newspaper powder agglomerates in the course of a screen analysis, and truly representative results of the particle size distribution are difficult to achieve. Disappearance of a gritty or lumpy feeling was chosen as the criterion. The following grinding procedure has been adopted:

1. Five passes through the grinder, followed by
2. 8 hours of ball milling.

The powdered newspaper product is a talcum-like, grit-free smooth powder. The particle size distribution is given in Table 11. Photographs of the newspaper, Figures 18-21, taken through a Leitz Dialux-Pol Microscope at 100x magnification show the gradual destruction of fibrous material and the crystalline nature of the resulting particles.

The use of such finely powdered newspaper has two advantages:

1. Clogging and blocking of check valves and lines in the small pilot plant is avoided.
2. Reactions can be studied in the absence of transport phenomena which would control for larger particle sizes.

It should be recognized that optimal particle size will be a key economic factor in a practical process and deserves further investigation.

SLURRY FEED PREPARATION AND PUMPING

In order to pump powdered newspaper feed through the system it is suspended in a carrier or vehicle. Besides facilitating pumping, a vehicle also serves to dilute the reactant mixture and prevents condensations to chars. Considerations for a vehicle are:

1. Thermal stability
2. Low vapor pressure
3. Solvent action
4. Low moderate cost.

Microphotographs of Newspaper

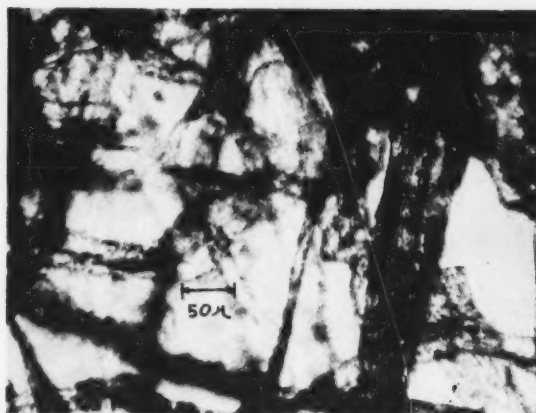


Figure 18. Torn newspaper
before grinding

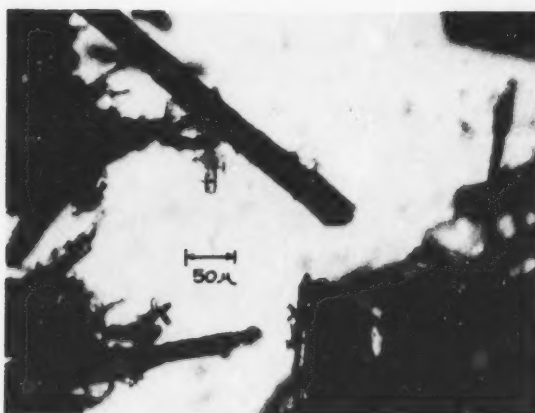


Figure 19. After five hammermill passes
and two hours ballmilling

Microphotographs of Newspaper

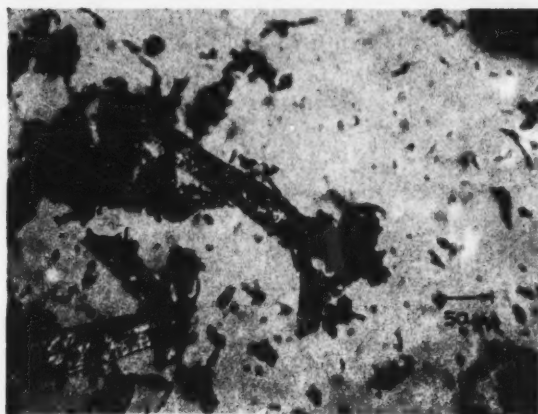


Figure 20. After five hammermill passes and four hours ballmilling

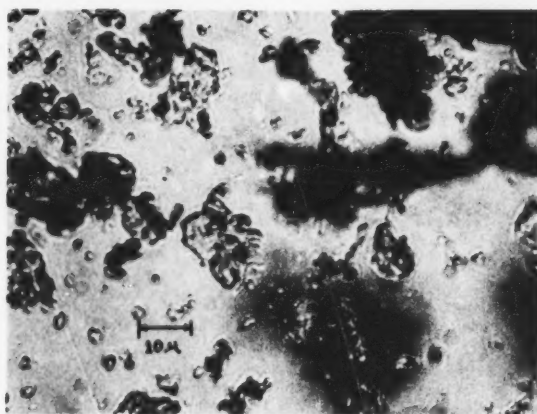


Figure 21. After five hammermill passes and eight hours ballmilling

Table 11. SCREEN ANALYSIS OF POWDERED NEWSPAPER FEED

Standard Mesh No.	Microns	% feed through screen
20	841	99.6
40	420	98.0
80	177	87.1
100	149	39.2
200	74	8.2

Water is a low cost vehicle, but, as its critical temperature is 375°C, to keep it in liquid phase below 375°C, one must operate at inordinately high pressures. A high boiling oil has not only a higher hydrogen solubility than does water, but it also permits independent variation of reactor temperature and pressure. The temperature limitation of 375°C no longer applies with oil. A study was made on the feasibility of a combination oil-water-newspaper slurry. In four separate experiments 50 grams of newspaper were wetted with varying amounts of water. 50 grams of oil were then added to these newspaper-water mixtures (the overall weight percent of water varied from 10-50%). It was observed that, as the percentage of water increased, the slurries became progressively thicker due to the swelling of the newspaper by water absorption. Thus, an oil carrier would seem to present a more suitable medium.

For initial experimentation, a paraffinic oil (see Table 12 for description) was chosen as the slurring vehicle. This oil is refractory to hydrocracking. More refractory would be a heavy hydrocrackate. The ideal oil would be that produced in the liquefaction process. Sustained operation to produce oil quantities sufficient for recycle use is needed.

The best solids content of the slurry was established by pumping slurries with increasing amounts of solid powder. (A graph indicating the variation of density with percentage slurry is shown in Figure 22.)

Table 12. NOMINAL SPECIFICATIONS OF WHITE MINERAL OIL
(No. 4434, Pennsylvania Refining Corp.)

Viscosity, SSU at 38°C	355
Specific gravity at 15.6°/15.6°	0.870
Flash Point, COC, °C	249
Pour Point, ASTM, °C	-17.8
Distillation Range (10 mmHg), °C initial to 95%	269°C-338
Bromine Number	Nil

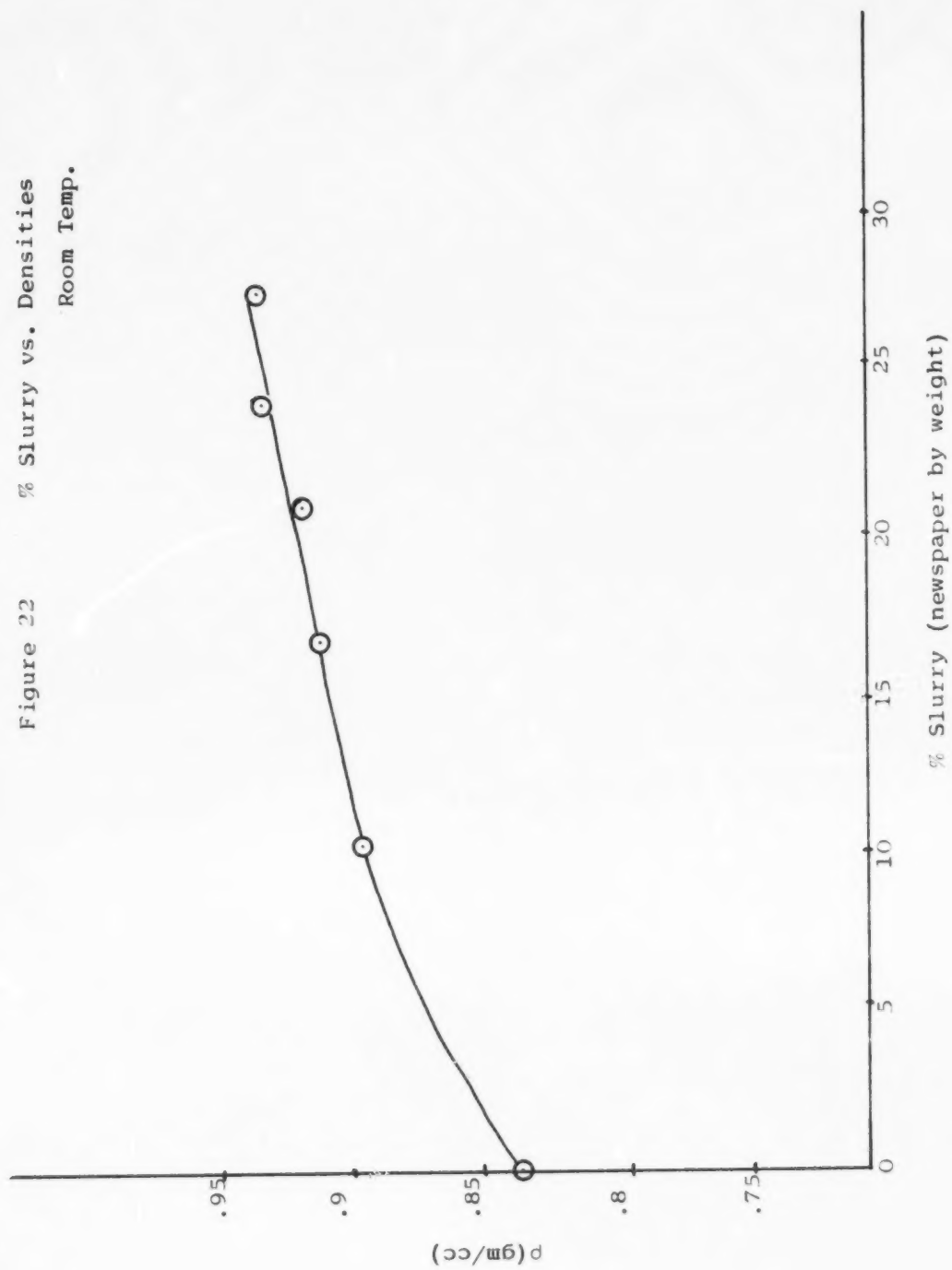
It was found that at 77°C a slurry of 25% powdered newspaper and 75% paraffin oil could be pumped without plugging of lines. Below 77°C a 25% slurry could not be pumped without plugging. At 77°C slurries with high solids content plugged consistently. The feed pump was calibrated at different slurry concentrations. Calibration curves are shown in Figures 23 and 24.

To get a better idea of the pressure effects encountered in the CSTR, the flow rate of a 20% slurry at a temperature of 78°C was studied using a high pressure receiver. This calibration curve is shown in Figure 25 and, of all the calibration curves, gives the most accurate representation of the actual flow rate into the CSTR.

HIGH PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

High pressure differential scanning calorimetry with hydrogen has the potential of being a rapid method for screening reactions such as cellulose liquefaction. Both endothermic (undesirable, tar forming) and exothermic

Figure 22 % Slurry vs. Densities
Room Temp.



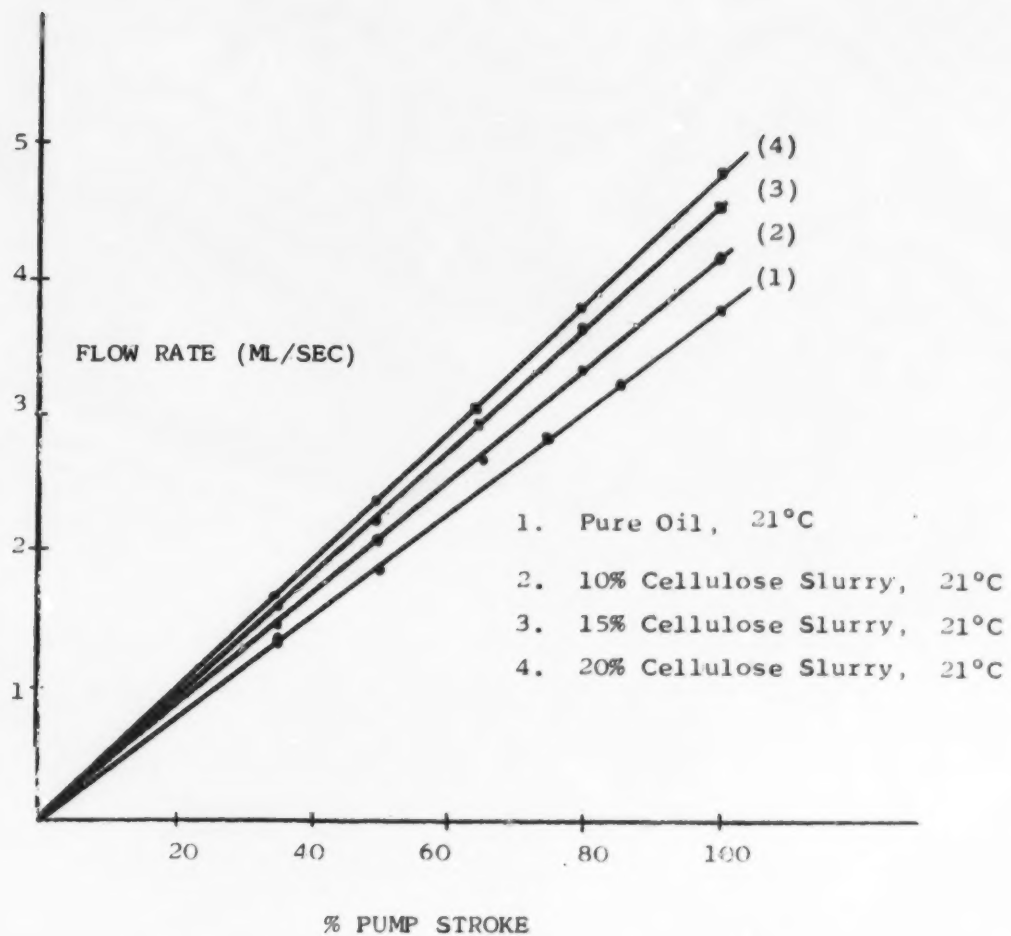


Figure 23: Calibration Curves for MilRoyal Pump
using slurries

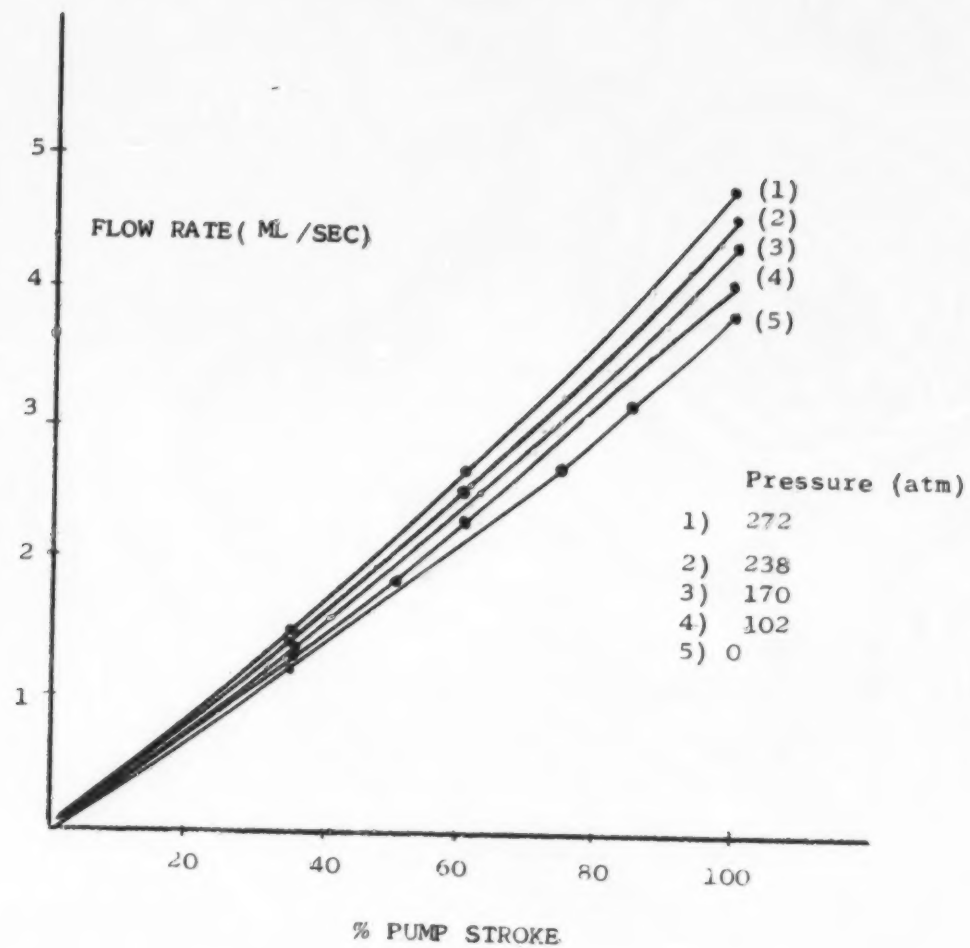
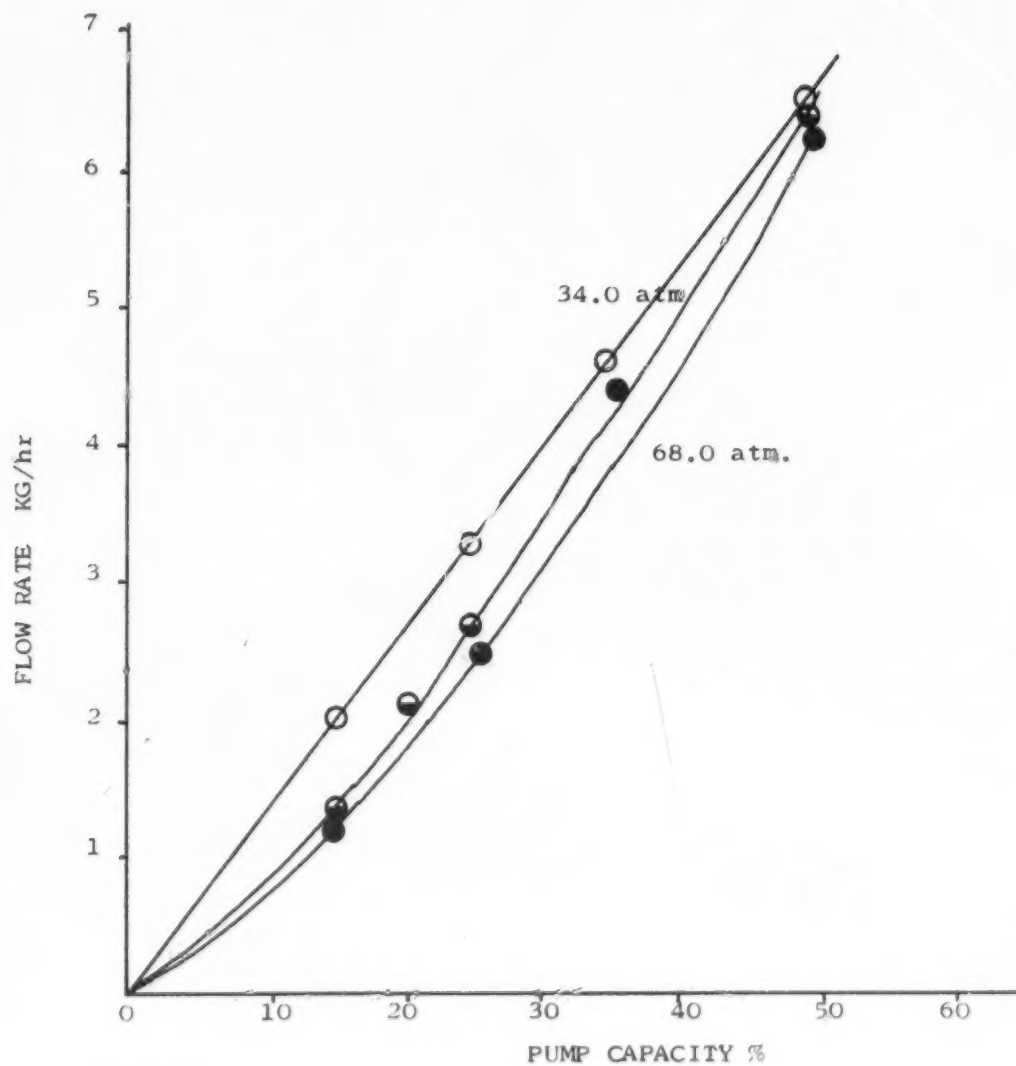


Figure 24: Calibration Curves for MilRoyal Pump
using Pure Oil at Room Temperature

Figure 25: Calibration curve for MR Pump
20% Newspaper in oil
Temp. = 78°C
High pressure receiver used



(desirable, hydrogenation) processes can be recognized and quantitated, as well as the temperature at which they occur. Catalyst screening can proceed effectively by this procedure.

The application of high pressure Differential Scanning Calorimetry (DSC) for micro-scale (1mg-10mg) screening of catalysts and model studies of process variables (gas composition, temperature, pressure) was investigated on a series on three samples: 1) powdered newspaper; 2) powdered newspaper (46%), mineral oil (48%), and platinum black catalyst (6%); and 3) cellulose (47%), mineral oil (46%), and platinum black catalyst (7%). Thermograms were obtained from D. David, Columbia Scientific Industries.

The samples were processed both in hydrogen and in helium at 129 atm. and were temperature programmed at 10°/min from 25°C to 450°C.

Absent from the thermograms of powdered newspaper (see Figures 26 and 27) is the expected endotherm at 350°C resulting from tar formation and the volatilization of levoglucosan. This observation had been reported by Halpern and Patai and confirmed by us.* In the presence of hydrogen, all samples (Figures 26-31) show a greatly enhanced lower temperature exotherm characteristic of hydrogenation.

The size of the hydrogenation exotherm from sample 3 (Figures 30 and 31) is no doubt related to both the increased size of the sample and the fact that newspaper contains only about 50% cellulose.

These results are quite promising and the quantitation of such data for catalyst selection has potential.

*In the case of sample 2 (Figures 28 and 29), the predicted endotherm is in fact present. Anomalies may well be due to the effect of platinum sample holders in these experiments.

Reference: 2mg Al_2O_3

Atmosphere 129 atm.

Sample Holder: DSC 202-3

Program Rate: $10^\circ/\text{min.}$

ΔT Gain: 80; 1.6 mcal/sec

Sample Weight 1.4 mg

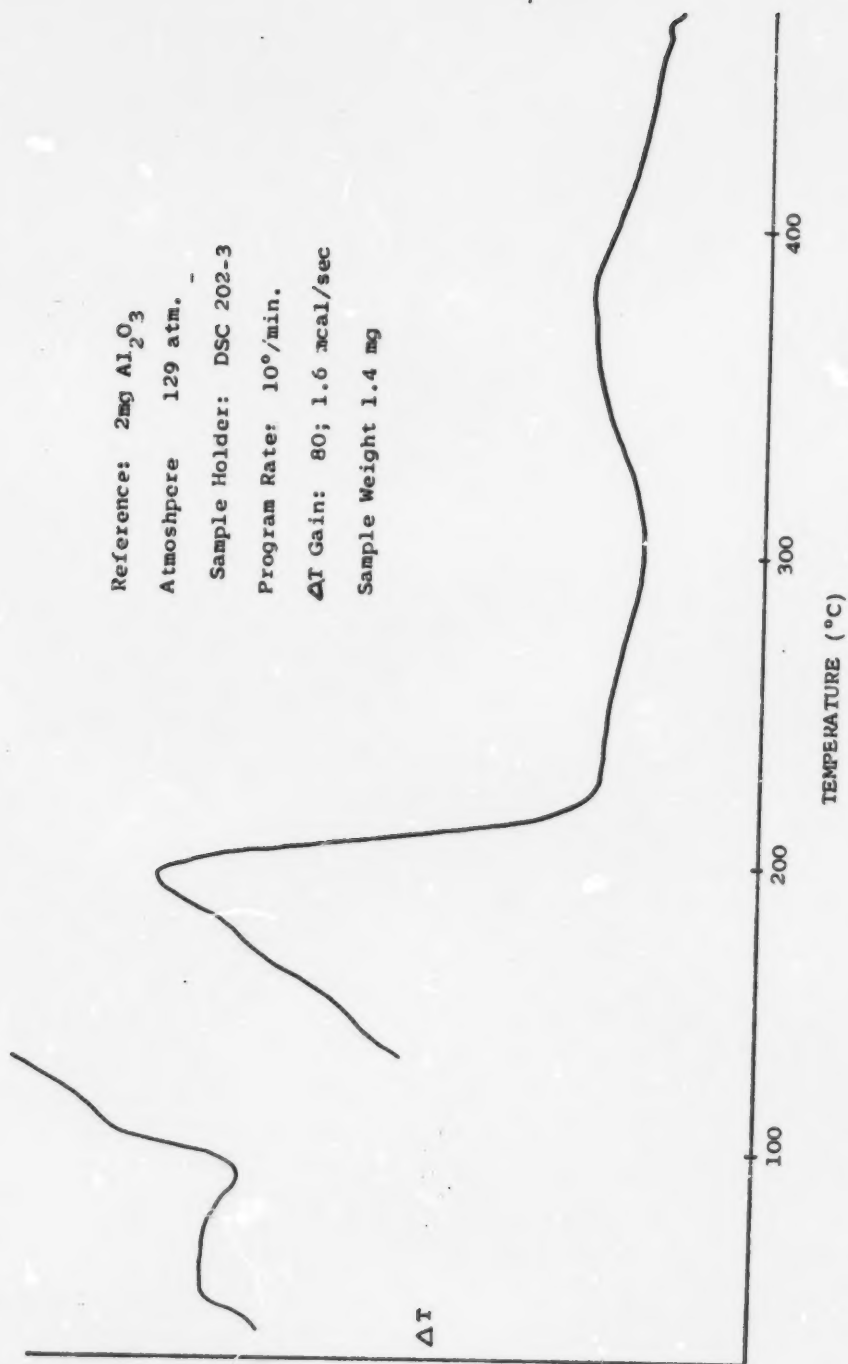


Figure 26: Thermogram of Powdered Newspaper in Hydrogen

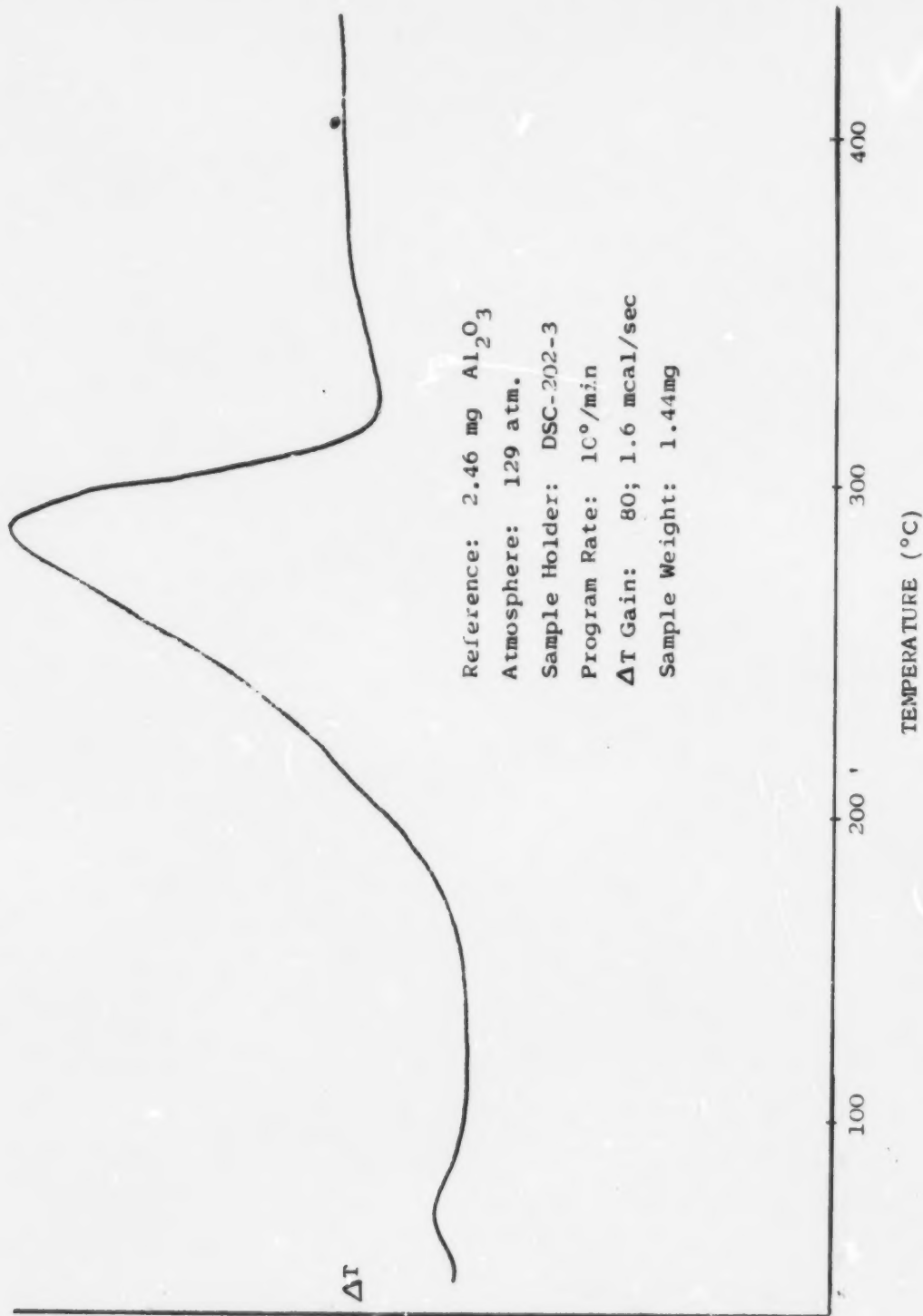


Figure 27: Thermogram of Powdered Newspaper in Helium

Reference: 3.51 mg Al_2O_3
Atmosphere: 129 atm.
Sample Holder: DSC-202-3
Program Rate: $10^\circ/\text{min}$
 ΔT Gain: 80; 1.6mcal/sec
Sample Weight: 2.83 mg

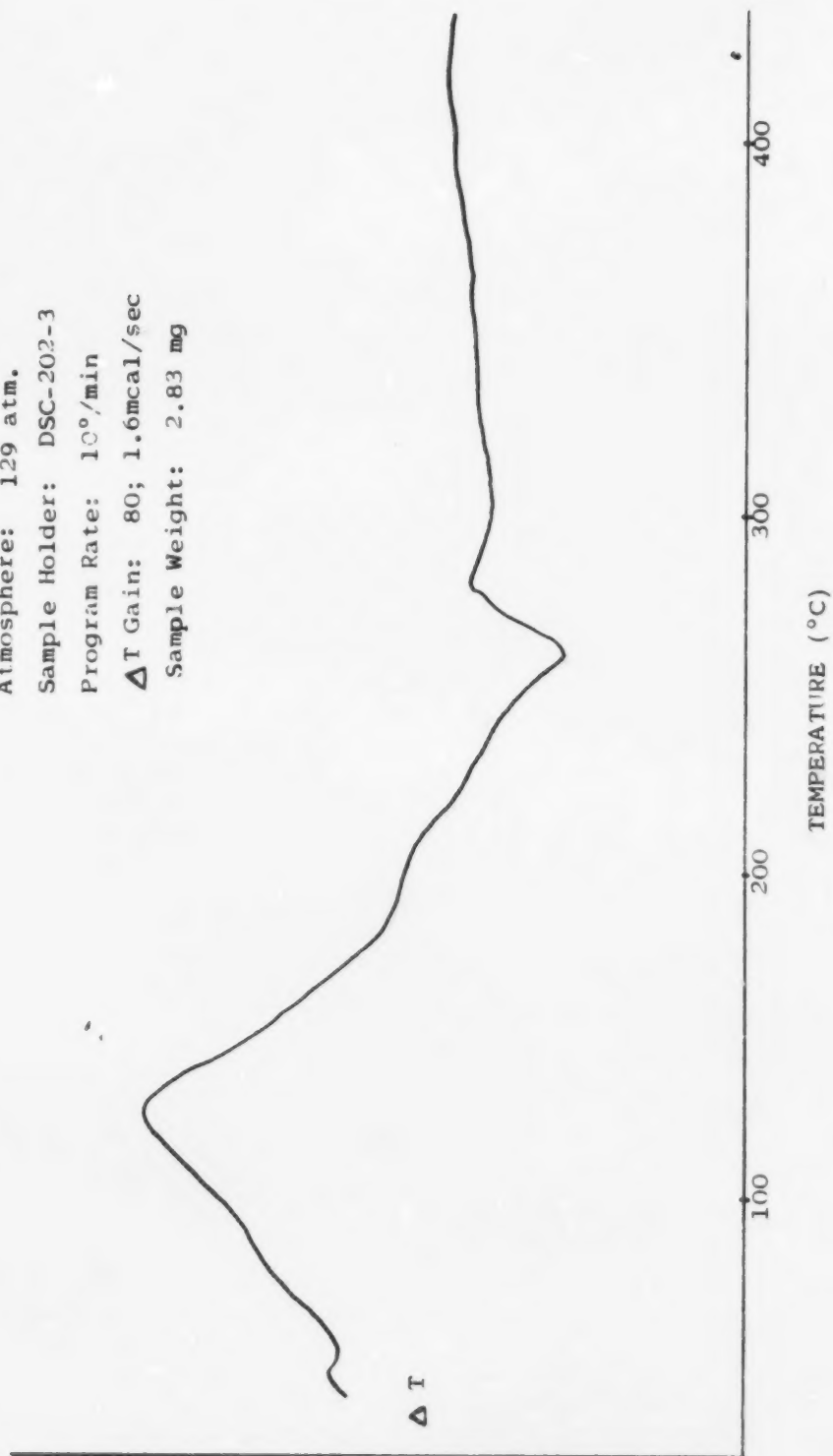


Figure 28: Thermogram of Mineral Oil . Newspaper and Catalyst (Platinum Black 5.1%)
in Hydrogen

Reference: 3.25 gm Al_2O_3
Atmosphere: 129 atm.
Sample Holder: DSC-202-3
Program Rate: $10^\circ/\text{min}$
 ΔT Gain: 80; 1.6 mcal/sec.
Sample Weight: 3.05 mg.



Figure 29: Thermogram of Mineral Oil, Powdered Newspaper, and Catalyst (Platinum Black 5.1%) in Helium.

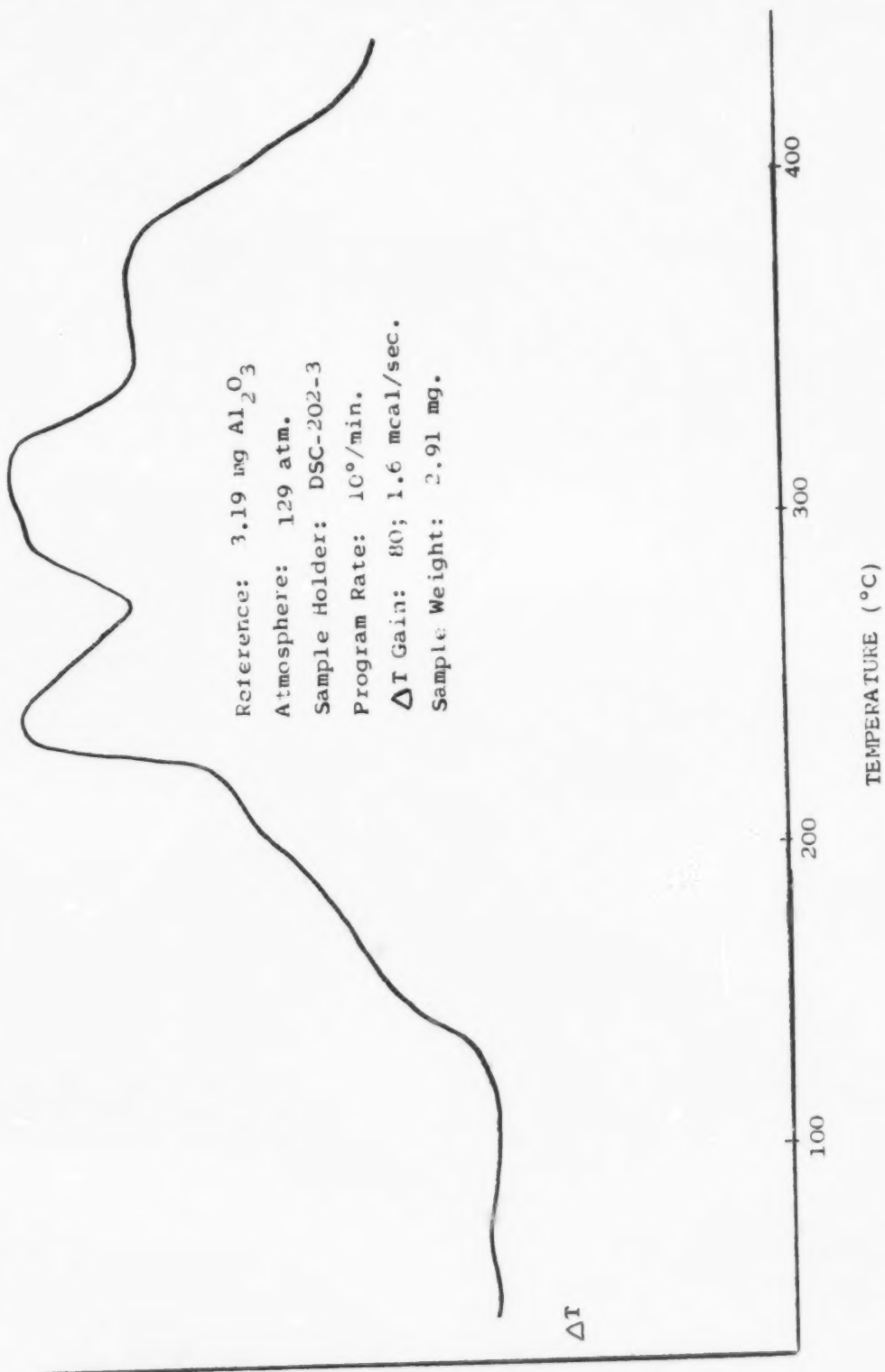


Figure 30: Thermogram of Mineral Oil, Cellulose, and Catalyst (Platinum Black 6.9%)
in Helium.

Reference: 3.7i mg Al_2O_3
 Atmosphere: 129 atm.
 Sample Holder: DSC-202-3
 Program Rate: $10^\circ/\text{sec}$.
 ΔT Gain: 80; 1.6 mcal/sec.
 Sample Weight: 3.11 mg.

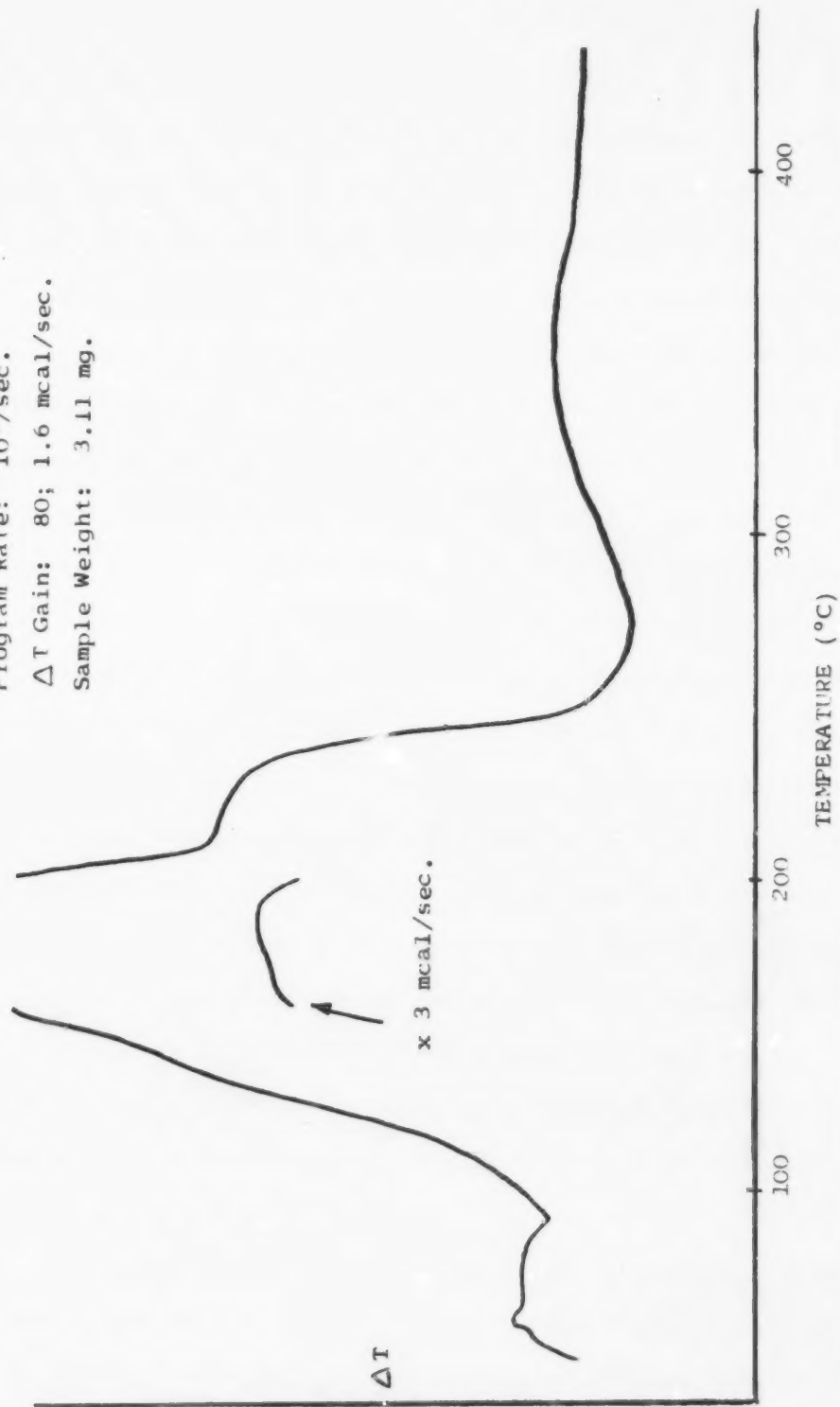


Figure 31: Thermogram of Mineral Oil, Cellulose, and Catalyst (Platinum Black 6.9%)
 in Hydrogen.

MICRO AUTOCLAVE TESTS

Initial catalyst screening experiments were performed in an 80cc micro autoclave heated by a Tecam fluidized sand bath with temperature regulated by a Honeywell temperature controller (see Figure 32). As constructed, the system permitted operation at maximum conditions of 343°C and 20.4 atm. The high pressure gaseous products were removed from the autoclave using the gas holding system shown in Figure 33 where they were stored for subsequent gas chromatographic analysis.

Two experiments were performed in this system at 343°C and initial hydrogen pressure at room temperature of 34.0 atm. One feed mixture contained 13.5 gm of carrier oil, 1.5 gm powdered newspaper, .023 gm Ni-Al alloy, .015 gm Ni on kiesulguhr, .026 gm nickel hydroxide and .015 gm nickelous nitrate hexahydrate. The other feed was made up of .9 gm of carrier oil, .0992 gm Ni-Al alloy, .1002 gm Ni on kiesulguhr, .1012 gm nickel hydroxide and .1006 gm nickelous nitrate hexahydrate.

The charged material was heated in the micro reactor from room temperature to 343°C over a period of approximately 50 minutes. The test on the feed containing powdered newspaper lasted for 15 minutes at 343°C. The other test had a duration of 1 hour 35 minutes at temperature. Cool down was accomplished using a second sand bath operated at room temperature, followed by a cold water rinse. The total cool down time was approximately ten minutes.

The data for these tests have been summarized in Table 13. A net increase in the amount of gas was obtained when the powdered newspaper was present. This was indicated by an increase of 2/3 atm. pressure at room temperature. A net increase in pressure suggests that pyrolysis of the newspaper into a char and light gases was occurring. Gas chromatographic

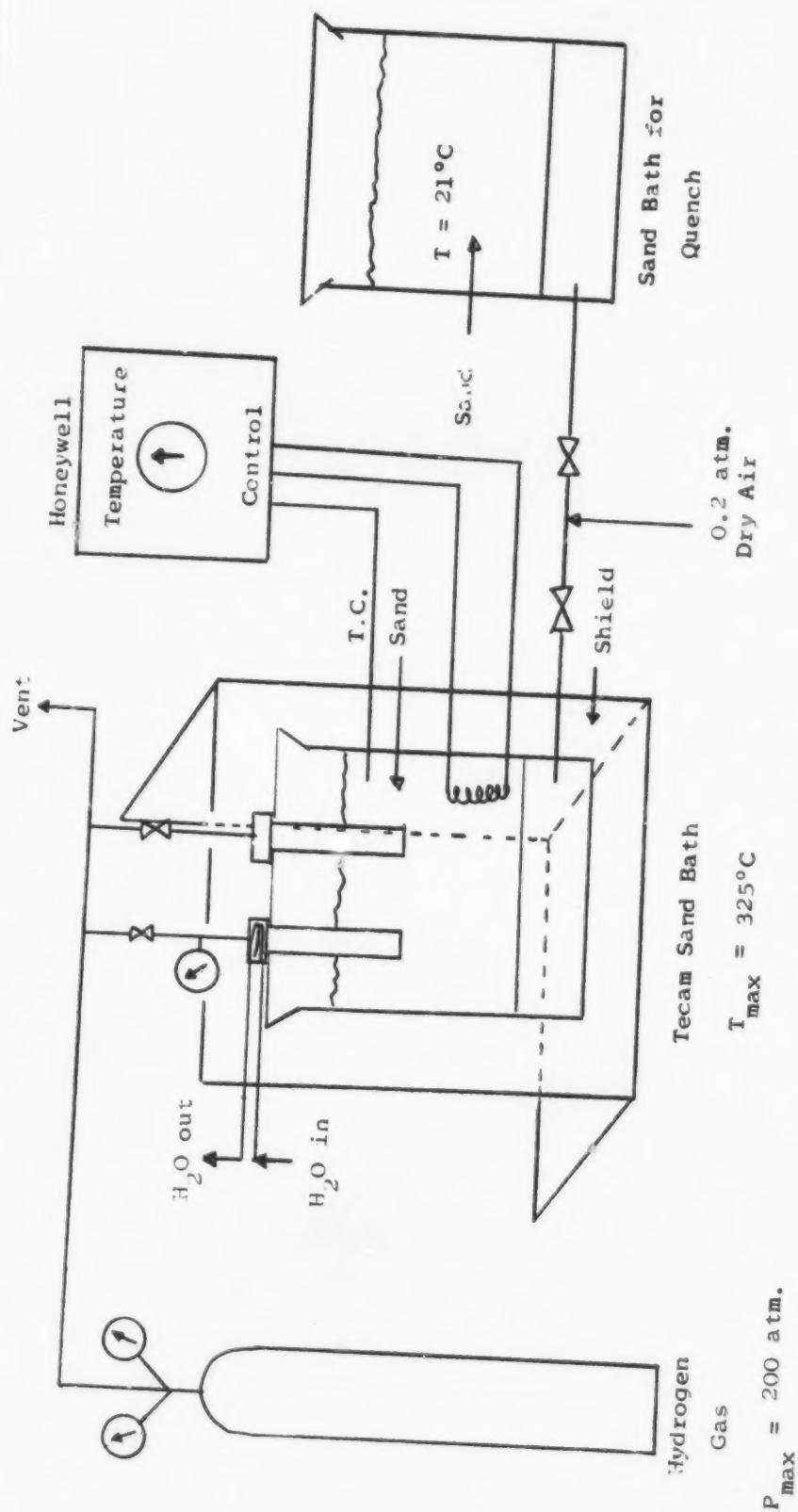


Figure 32: Batch Autoclave System

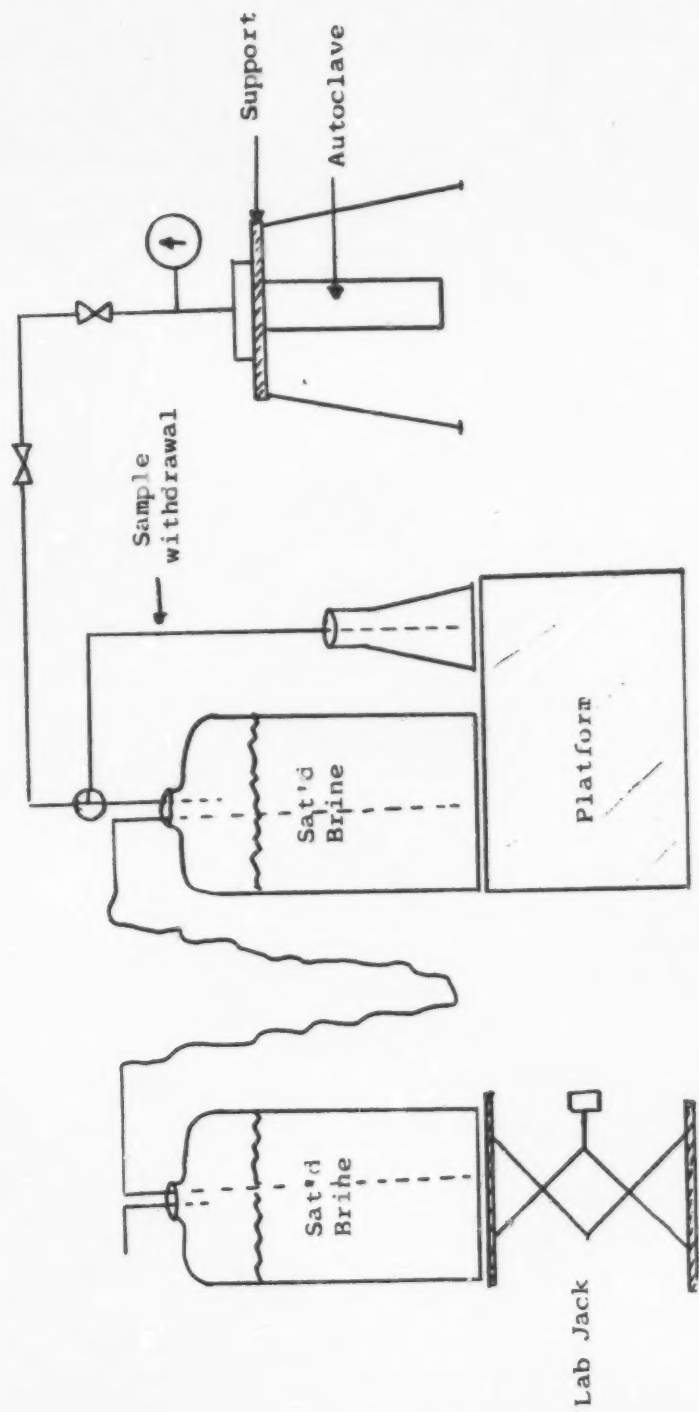


Figure 33: Gaseous Product Holding System For
Batch Autoclave.

Table 13. MICRO AUTOCLAVE TEST DATA

Oil gm	Feed		Total Catalyst gm	Press at RT		Reaction Temp °C	% Conv. Newsaper (DAF)	Insoluble residue gm
	Newsaper gm			init ^c atm	final atm			
13.50	1.50		.079 ^a	34.0	34.6	343	55.6%	0.73
.87	--		.401 ^b	34.0	32.3	343	---	---

^aNi(OH)₂ - .026 gm, Ni(NO₃)₂·6H₂O - .015 gm, Ni-Al Alloy - .023 gm, Ni on Kiesulguhr - .015 gm

^bNi(OH)₂ - .1012 gm, Ni(NO₃)₂·6H₂O - .1006 gm, Ni-Al Alloy - .0992 gm, Ni on Kiesulguhr - .1002 gm

^cAutoclave pressured initially with H₂

analysis of the product gas using a 10' x 1/8" stainless steel column containing MCV molecular screening carbon showed that carbon dioxide and carbon monoxide were present and this was the most important finding of the work, that the water gas shift reaction could proceed in the reaction system.

The condensed phases were separated by soxhlet extraction using benzene, acetone, and methanol successively. The extracts were concentrated using a vacuum rotary evaporator and analyzed by gas chromatography on a 3' x 1/8" stainless steel column containing 20% SE-30 on Chromosorb W. The chromatograms were complex and indicated the presence of numerous components. The solid residue weighed 0.70 gm and represented a 52% conversion.

Because pyrolysis was occurring, it was felt that poor liquid-gas contact, settling of the solids in the charge, and low reaction temperature were affecting the results and causing poor reaction selectivity, i.e., pyrolysis instead of hydrogenolysis. In order to remedy these problems smaller samples should be processed (1-2cc) and a bronze block heater (maximum temperature greater than 540°C) mounted on a vibrator was fabricated to heat and agitate the reactor.

ROCKING AUTOCLAVE STUDIES

An Aminco micro series high pressure shaking assembly with a 2-9/16" o.d. 300 cc autoclave was used to screen catalysts and to determine suitable operating conditions for the formation of liquid hydrocarbons from powdered newspaper. The autoclave has a maximum pressure capacity of 560 atm. at 427°C. The volume with pyrex liner in place is 250cc and liquid samples as large as 100 cc may be used. The shaking assembly rocked the autoclave from 30 degrees above the horizontal to 30 degrees

below. A 1 Kw heating jacket connected to a -18°C to 1090°C Wheelco temperature controller was used to maintain the temperature of the reactor. Pressure was monitored by a 0-227 atm. Honeywell Pressure Recorder.

The results obtained from the tests using this equipment will guide the operation of the CSTR.

EXPERIMENTS WITH POWDERED NEWSPAPER

An initial study has been performed on a mixture of nickel catalysts. The mixture was made up of three forms of nickel, namely, nickel hydroxide, nickel on Kieselguhr, and Ni-Al alloy.

Mixtures containing carrier oil, powdered newspaper, and catalyst, stirred at 30°C for at least one hour, were used to charge the reactor. Table 14 contains the catalyst feed composition as well as the total charges for each run. The total catalyst weight amounts to 5% of the weight of newspaper present in the sample. Several blank runs containing mineral oil and hydrogen were conducted in conjunction with studies on sewage sludge.

The operating conditions examined were temperatures of $371-399^{\circ}\text{C}$ with maximum pressures of approximately 95 atm. These pressures resulted from an initial charge, at room temperature, of about 47.6 atm. of either hydrogen or nitrogen gas. A heat up period ranging between $1\frac{1}{2}$ to 2 hours was required to reach the desired temperature, which was maintained for 1 to 2 hours. The cooling period required to reduce the temperature to about 121°C was approximately 2 hours. Temperature and pressure as a function of time have been plotted as Figures 34-37.

Figures 34, 35, and 36 are plots for tests in H_2 atmosphere on powdered newspaper plus oil, powdered newspaper plus oil plus catalyst, and oil plus

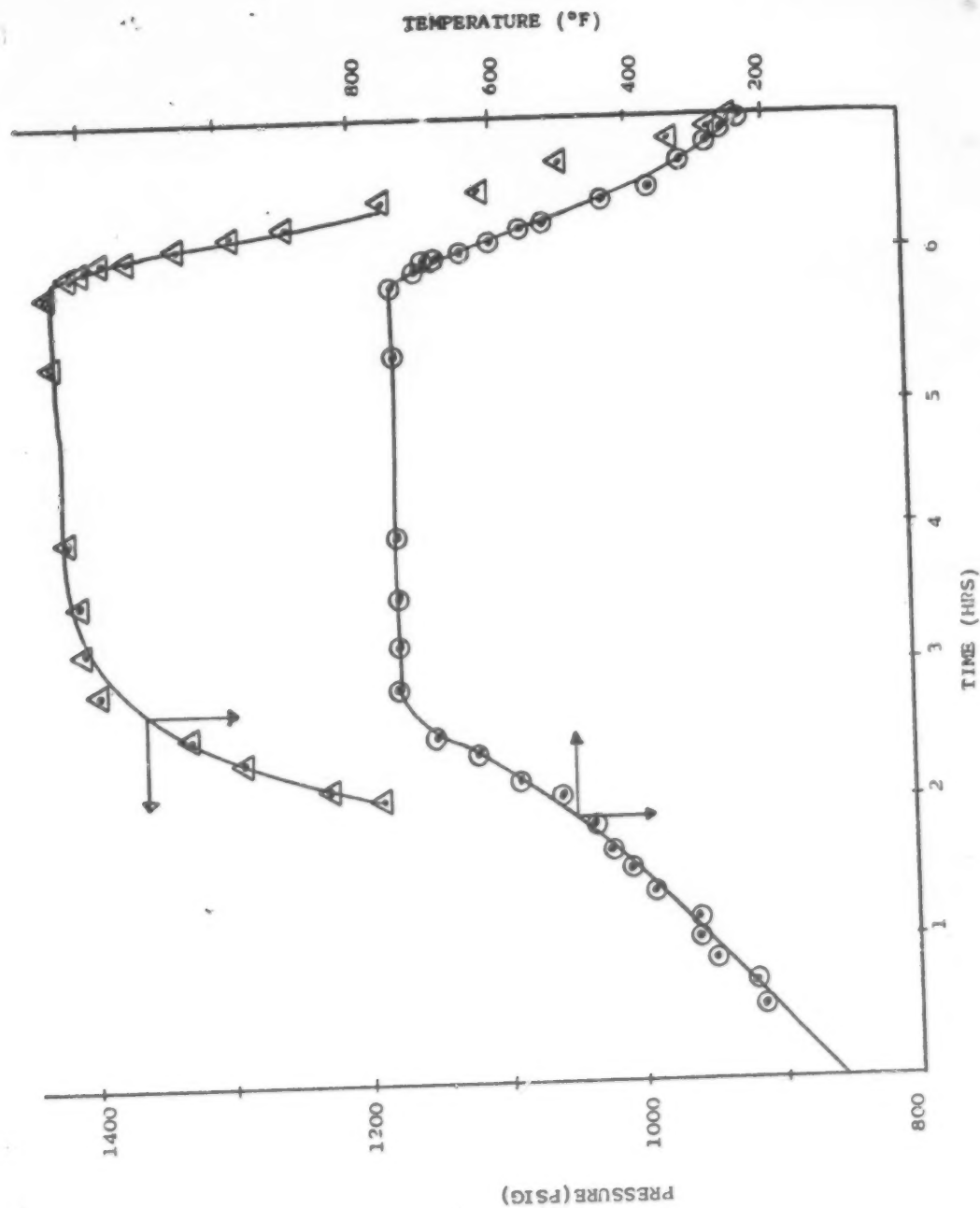


Figure 34: Temperature-Pressure vs. Time Plot; Run 1
Powdered Newspaper, Mineral Oil, and Hydrogen

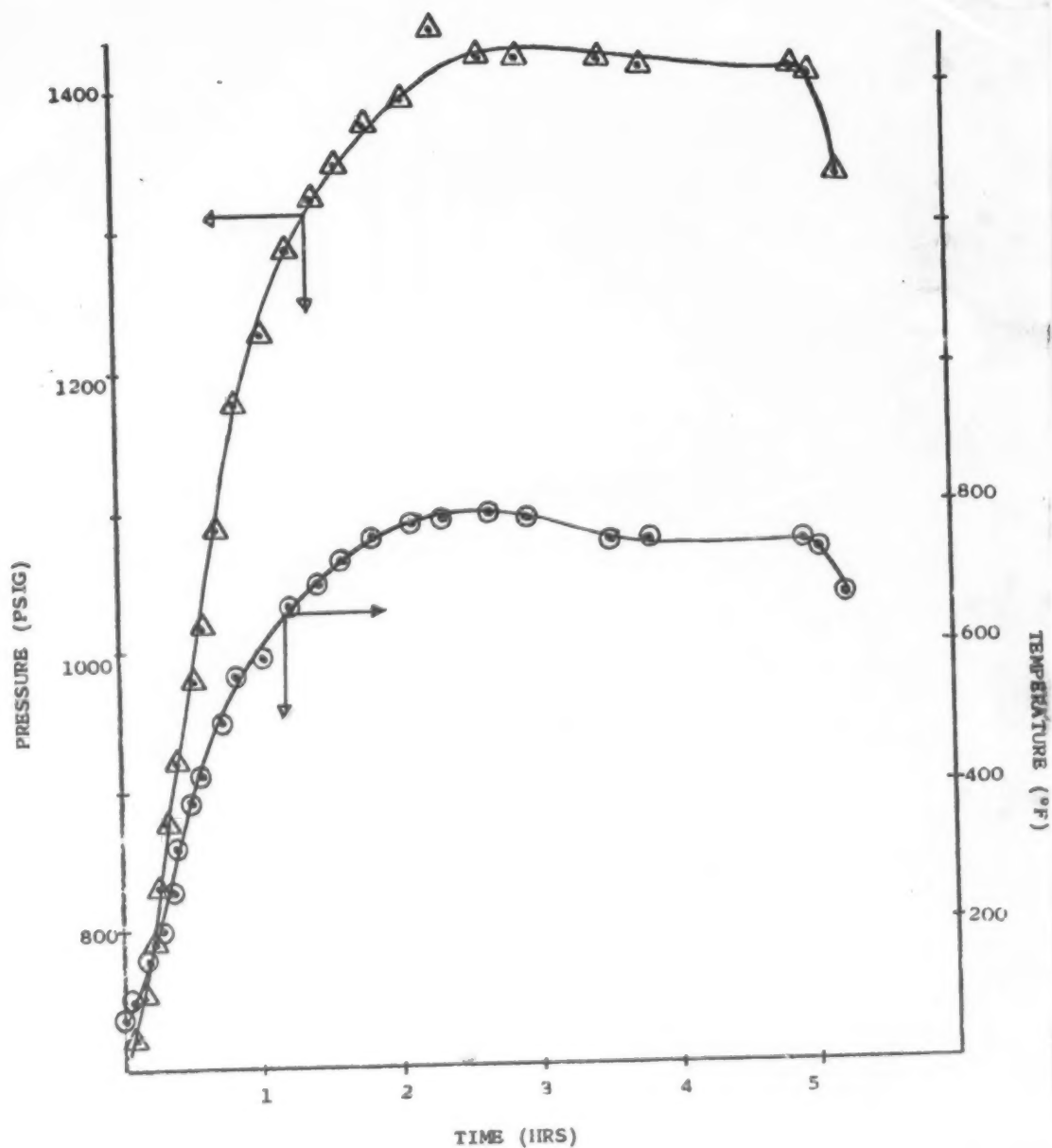


Figure 35: Temperature-Pressure vs. Time Plots;
Run 2; Powdered Newspaper, Mineral Oil, Catalyst
and Hydrogen.

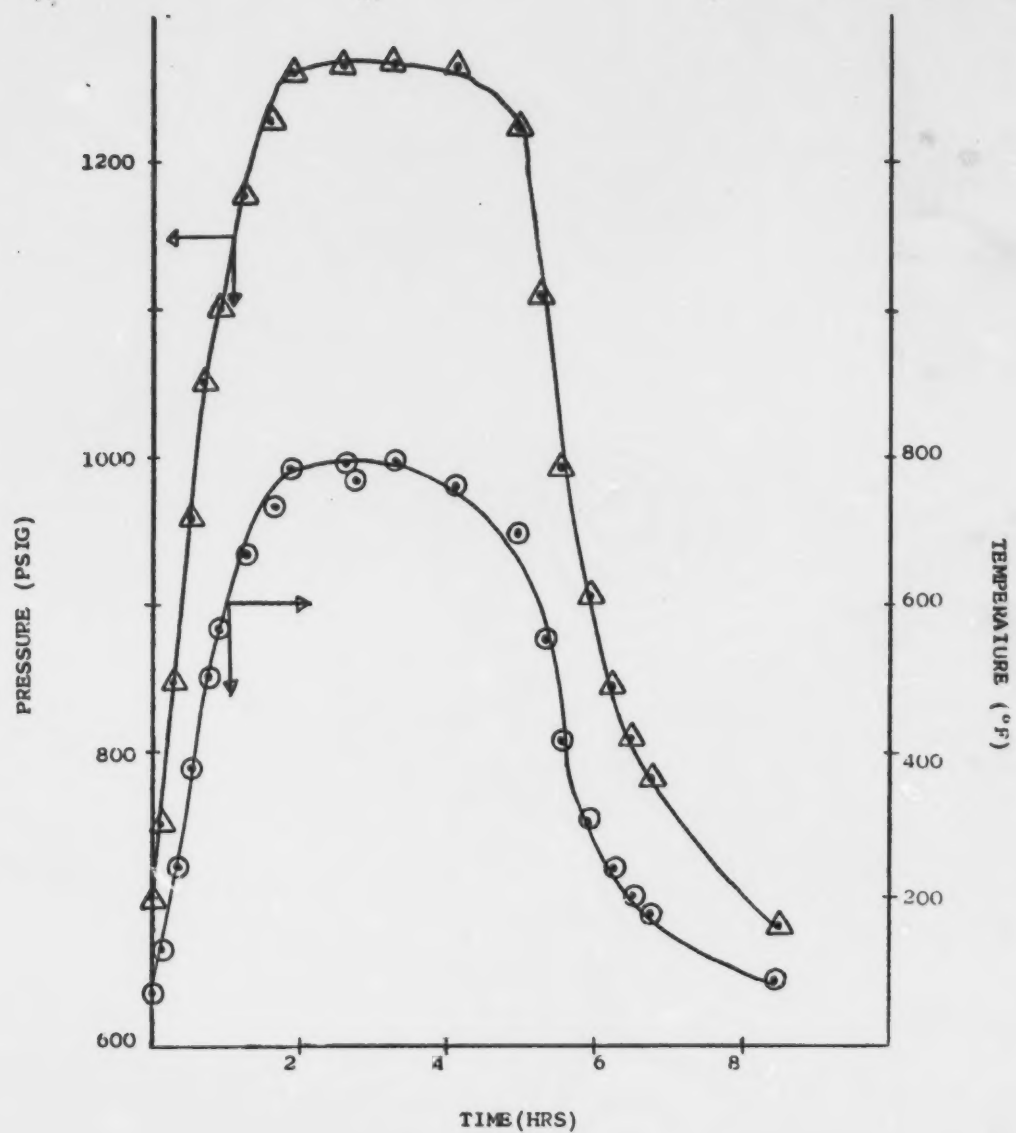


Figure 36: Temperature-Pressure vs. Time Plot;
Run 3; Mineral Oil, Catalyst and Hydrogen

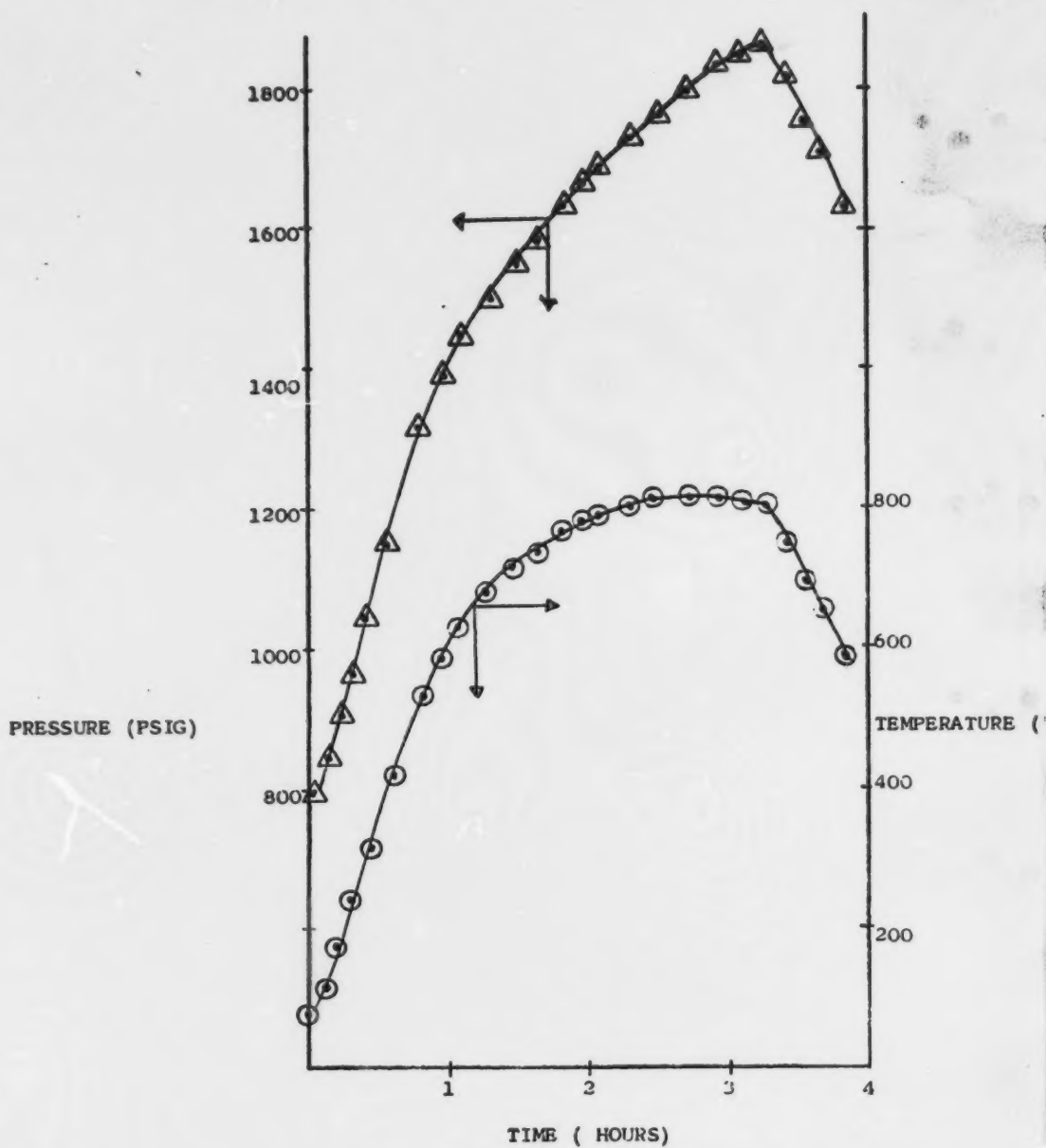


Figure 37: Temperature-Pressure vs. Time Plot;
Run 4; Powdered Newspaper, Mineral
Oil, Catalyst, and Nitrogen.

Table 14. ROCKING AUTOCLAVE CATALYST MIXTURES

Run	Ni(OH) ₂ ^a Grams/Gram Carrier Oil	Ni-Al Alloy ^b	Ni on Kieselguhr ^c	Total Charge
1	----	----	----	19.25
2	.00442	.00442	.00442	22.46
3	.00427	.00427	.00427	15.69
4	.00442	.00442	.00442	21.9

^aPpt from Ni(NO₃)₂·6H₂O by NH₄OH then dried at 104°C for 1 hour

^bHarshaw Ni catalyst 50-50 Ni-Al

^cCrushed Girdler G-53 pellet. Particle size 500 microns

catalyst, respectively. For these, no unusual pressure behavior was readily noticeable, i.e., a variation in temperature had a corresponding variation in pressure. The final plot (Figure 37) represents the temperature-pressure behavior in a N₂ atmosphere for powdered newspaper plus oil plus catalyst. A sharp rise in pressure occurred while the temperature remained constant signifying a net production of gaseous products. This observation was substantiated by the net rise in pressure of 3.36 atm. from reactants to products measured at room temperature. This represents a net gain of 0.032 moles of gaseous phase. In contrast, the test conducted on a similar charge in a H₂ environment suffered a decrease in pressure of 4.35 atm., a net loss of 0.048 moles. These results suggest a significant hydrogen consumption was effected by the mixture of nickel catalysts in the presence of hydrogen gas.

Physical separation of the condensed phases was accomplished by suction filtration through a porcelain crucible with an 8.8 micron sintered glass bottom. Before filtration, the total condensed phases were diluted with 50 cc benzene to aid in their removal from the reaction vessel and to facilitate the filtration. The weights of solid residue as well as that of the total condensed phases were obtained and are listed in Table 15.

Table 15. ROCKING AUTOCLAVE PRODUCTS

Run	Total condensed Phases gm.	Insoluble Residue ^a gm	% Solid ^b residue	Final Pressure at Room Temp. atm.
1	17.77	1.12	29.8	48.6
2	20.54	.39	3.5	43.7
3	14.48	----	----	45.4
4	20.40	1.85	36.2	56.7

^a Insoluble in benzene at room temperature

^b Based on initial weight of newspaper

The percent residue based on initial newspaper was found for each experiment. The values ranged from 36.2% when nitrogen gas and nickel catalyst were used to 3.5% when hydrogen gas and nickel catalyst were used. The residue when no catalyst was used was 29.8% of the initial newspaper charge weight. The 3.5% residue indicates that newspaper was converted almost entirely to liquid or gaseous products.

Table 16 summarizes the rocking autoclave results. This table lists the conditions of the experiments, the percent residue based on initial newspaper, and the change in the amount of condensed phases. A qualitative

Table 16. INITIAL RESULTS OF ROCKING AUTOCLAVE TESTS^{a, b}

Run	Feed ^c Composition gm/gm oil Newspaper ^d Ni Cat.	Total Charge gm	Temp °C	Press at Room Temp. Init. Final atm atm	Charge Gas	Max Press atm	% Solid residue	Condensed Phase wt. change (gm)
1	.242	----	390	47.8 48.6	H ₂	97.2	29.8	1.48
2	.250	.01326	402	48.1 44.6	H ₂	97.1	3.5	1.92
3	----	.01281	410	47.3 45.4	H ₂	116.2	---	1.21
4	.250	.01326	427	53.8 57.0	H ₂	117.8	36.2	1.50

^aDuration of runs 1-2 hrs.

^bHeat up period 1½-2½ hrs. Cool down to 121°C 2 hrs.

^cSee Table 18 for detailed description of feed charges

^dMoisture content 3.85%

^eBased on initial weight of newspaper

analysis of the gas phase indicates that the gas products formed were carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, propylene, n-butane, isobutane, isobutylene, trans and cis butene-2 and unidentified C-5 hydrocarbons (see chromatogram, Figure 38).

Catalyst Screening

The catalyst screening experiments were conducted at 371°C for one hour (100-170 minutes required for heat up, 1 hour hold) with an initial hydrogen pressure of approximately 47.6 atm. Powdered newspaper was used as the model feed and catalyst loading was 5% based on the weight of the newspaper. At conditions slightly more severe than these (427°C, 140 minute heat up with no hold) a conversion approaching 100% was reached. When this occurred, it was difficult to determine at what point conversion had stopped taking place. On the other hand, when 371°C was used as a maximum temperature, with no constant temperature period, a low conversion (68.2%) was obtained. This resulted from the fact that not enough time was allowed for reaching the 90% conversion level. The intermediate severity of 371°C held for one hour at constant temperature provided the desired conversion while making it reasonably certain further conversion could be obtained.

Twelve different catalysts were examined in this study. Their effectiveness was determined by comparing the percentage residue (DAFB) obtained under the previously described standardized reaction conditions. The source and preparation for each of the catalysts is described briefly below.

Column: Durapak-n-octane, Porasil
 Detector: 200°C; 200 mg.
 Injector: 150°
 Carrier: Helium at 60 cc/min.
 Program: 60°C (0-3 min) 60° → 100° at 10°/min.
 Sample Size: 1.00 cc.

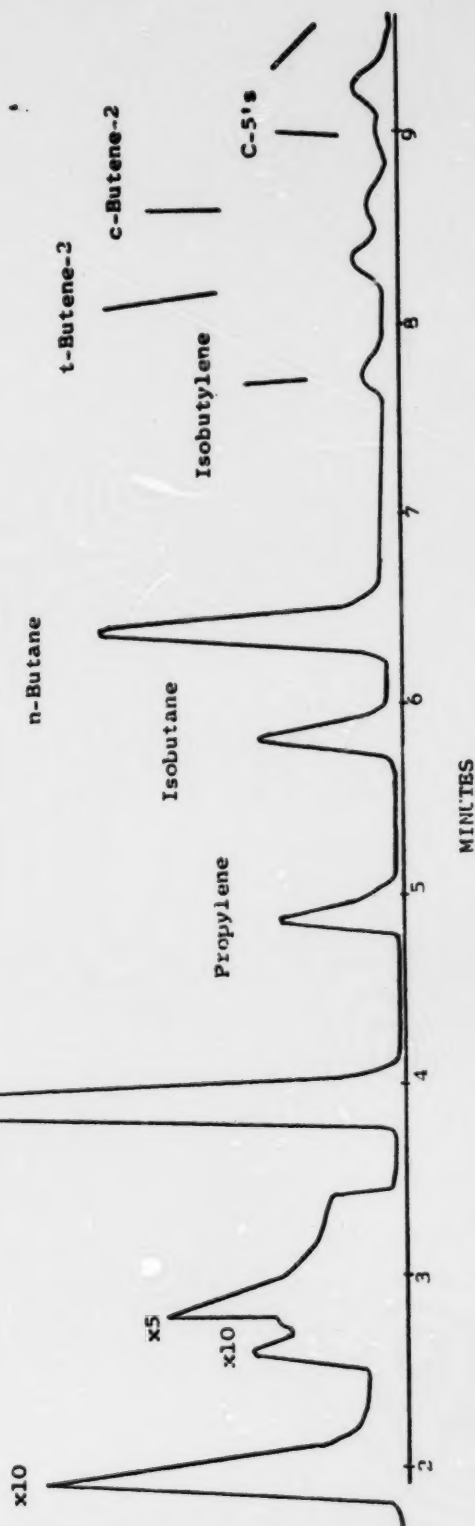


Figure 38: Gas Chromatograms of Gaseous Products from Run 2
 Mineral Oil, Powdered Newspaper, Hydrogen Catalyst

Nickel Hydroxide - Freshly precipitated nickel hydroxide was used. This was prepared by dissolving nickelous nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium hydroxide (NH_4OH) in water and then heating to drive off the ammonia, causing the formation of a green precipitate. This was filtered, dried, and powdered. The nickelous nitrate and ammonium hydroxide were both "Baker analyzed" reagents with lot numbers 26844 and 38820 and nominal purities of 99.0% and 28.0 to 30.0%, respectively.

G-53 - A Girdler catalyst generally used for difficult hydrogenations, G-53 is a chemically precipitated nickel catalyst, supported on Kieselguhr, dry-reduced and suspended in a protective medium of hardened tallow or edible oil. Nominal composition: 25% Ni, 15% Kieselguhr, 60% protective medium. The granules were ground so that all the material passed through 80 mesh screen.

Ferric Sulfate - A powdered iron (3) sulfate hydrate manufactured by J.T. Baker. "Baker analyzed" reagent lot no. 39784; nominal purity 73.0%.

Ferric Oxide - A powdered iron (III) oxide also manufactured by J.T. Baker. Lot no. 36473, 98.0% pure.

Iron Sulfide - Technical grade FeS which had been ground using a mortar and pestle.

Cobalt-Molybdenum - Aero HDS 1441 manufactured by Cyanamid Company. It is a cobalt-molybdenum catalyst with the following composition: 3% cobalt oxide, 15% molybdenum oxide, 3% silica. Ground to pass through 60 mesh screen.

G-51 - G-51 is a cobalt-molybdenum catalyst on a high purity gamma alumina support. It was obtained from Chemetron Corporation as pellets and ground to pass through 60 mesh screen before use.

G-67RS - Reduced and stabilized Zirconium promoted cobalt on Kieselguhr containing 60% cobalt from Girdler. This catalyst also passed through 60 mesh screen.

G-61RS - Similar to G-67RS but without Zirconium promoter.

Millscale - Scale from low carbon steel containing all oxides of iron. Supplied by Fairless Works of U.S. Steel.

Zeolite Cracking Catalyst - Supplied by U.O.P. Research Center and used as received.

Nickel Carbonate - Manufactured by C.A.F. Kahlbaum; ground to pass through a 60 mesh screen before use.

Results

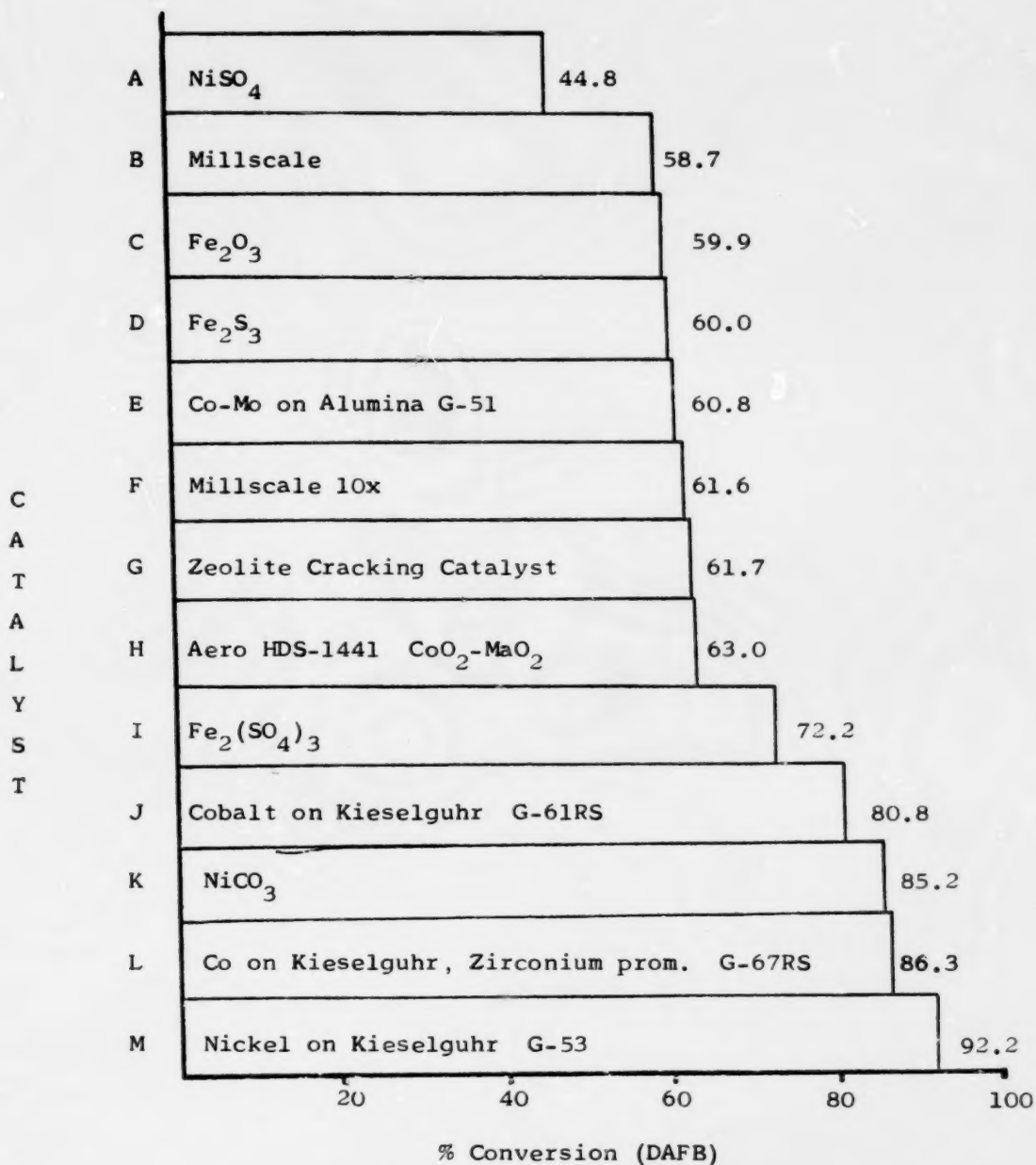
The results of the catalyst screening studies are summarized in Figure 39 while Table 17 contains representative experimental data.

Several forms of nickel and cobalt catalysts at 371°C effected significant conversion of powdered newspaper, and, in fact, the highest percentage residue for the catalyzed experiments occurred when nickel sulfate was used.

In order to understand nickel sulfate in activity, it should be noted that the effective catalysts appeared to share two characteristics. It is believed that each was present in reduced form or was reduced in-situ. and that each was distributed over an extended surface or was present as a finely divided powder. It has been reported in the literature (18) that nickel carbonate reduces to a finely divided nickel at temperatures above 300°C in the presence of hydrogen. On the other hand, the chemetron G-53, G-61RS, and G-67RS catalysts are commercially prereduced and stabilized forms of nickel and cobalt dispersed on high surface area supports.

Figure 39. CATALYST SCREENING AT LOW SEVERITY

47.6 atm; 371°C; 100 minutes heat-up;
60 minutes hold; catalyst loading 5%^a



^a based on weight of powdered newspaper

Table 17. CATALYST SCREENING AT LOW SEVERITY

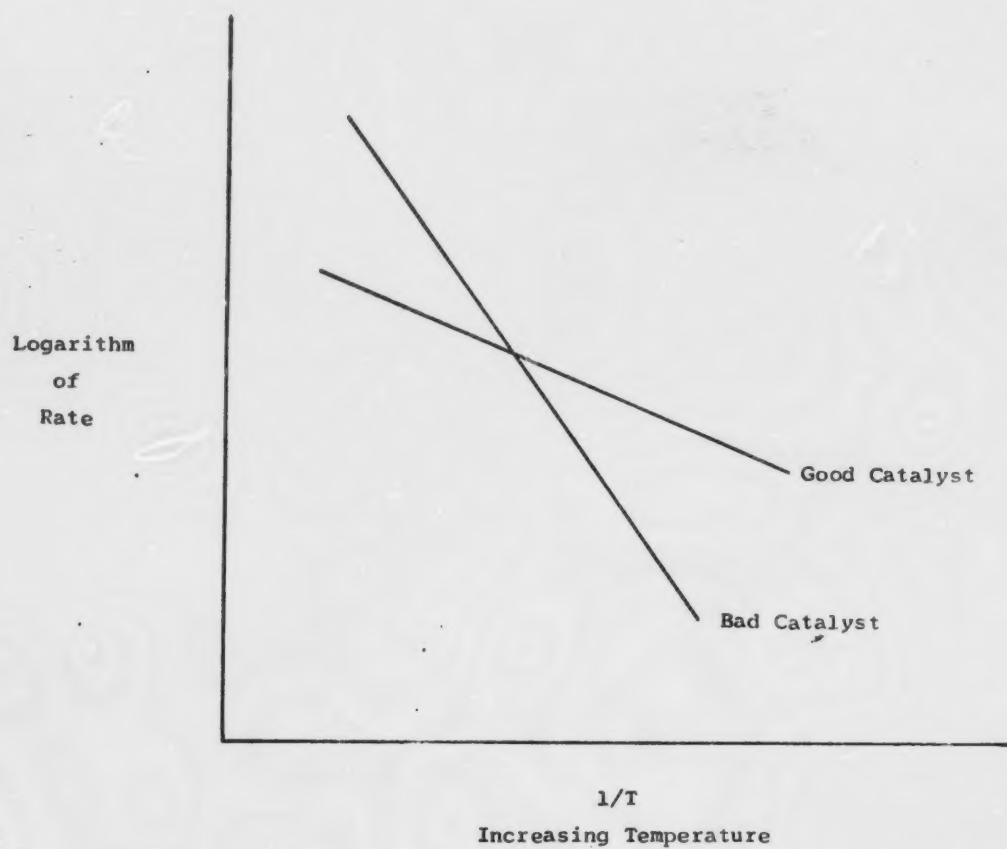
Cat.	Feed (gm)		Gas (atm)	Heating (min)		Pressure(atm)		Recovery	ΔH_{comb}				
	Solid	Oil		Cat.	Up	Hold	Tmax(°C)			Max.	Final	Condensed	Solids
(A)	4.58	18.4	0.229	46.4	100	60	378	92.2	46.7	22.00	3.035	44.8	20,000
(B)	4.66	18.61	0.233	47.2	170	75	376	90.5	Leak	21.20	2.35	58.5	19,600
(C)	5.18	20.88	0.278	49.0	170	60	377	103	48.9	24.33	3.00	59.9	20,000
(D)	4.13	16.51	0.206	50.3	120	60	378	98.2	50.7	18.89	1.70	60.0	
(E)	4.71	18.90	0.24	48.2	120	60	372	92.5	49.6	22.60	2.80	60.8	19,650
(F)	4.40	17.55	2.17	48.3	105	60	374	97.3	48.6	22.94	4.45	61.6	20,000
(G)	4.87	19.00	0.23	39.2	94	55	388	78.2	41.8	22.44	2.01	61.7	19,200
(H)	5.97	24.03	0.31	48.0	118	60	374	93.9		24.72	3.15	63.0	
(I)	4.07	16.38	0.251	47.0	170	60	378	87.0	47.0	18.60	3.25	72.2	19,450
(J)	4.87	19.79	0.241	48.0	100	60	381	80.6	Leak 27.1	23.50	1.492	80.8	19,900
(K)	4.59	18.37	0.225	47.2	100	60	372	68.1 ^{Leak}	23.1	21.50	0.865	85.2	
(L)	4.71	19.41	0.241	48.0	135	60	378	89.5	45.4	23.01	1.03	86.3	19,400
(M)	4.92	19.7	0.269	38.1	105	55	371	72.1	35.6	23.67	0.802	92.2	

Examination of the conditions of the nickel sulfate catalyst experiments reveal two possible deficiencies which explain nickel sulfate's low activity. The first is the use of crushed nickel sulfate crystals which could have been poorly dispersed possibly causing reduced catalytic effectiveness. The second was the possibility that only a limited degree of reduction of nickel sulfate to nickel metal occurred. Pannetier and Abegg (80) studied the reduction of nickel sulfate heptahydrate in the presence of hydrogen gas at temperatures of approximately 350°C. They found that only traces of nickel metal were formed and that the major product was Ni_3S_2 . They also found that increased temperature in the presence of water favor the formation of nickel metal. These results, then, support an hypothesis of incomplete reduction and suggest that greater effectiveness may be obtained by increasing temperature while providing additional water.

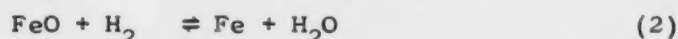
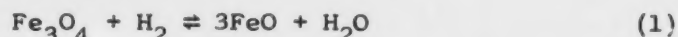
A disappointing result was the inability of the iron catalysts to effect substantial conversion to liquids and gases. The ferrous catalysts were attractive because of their comparatively low cost, but, as is apparent, they were unable to catalyze the liquefaction reaction at 371°C.

Two reasonable explanations can be given to account for iron's lack of activity. The first is the possibility that iron is a poorer catalyst than both nickel and cobalt, thus having a higher activation energy. Figure 40 shows an activation energy plot comparing a good and bad catalyst. It is interesting to note that, although the poorer catalyst shows little activity at low temperatures, the activity may eventually exceed that of a better catalyst when the temperature is raised. For this reason, tests should be conducted on the iron catalysts at temperatures above 371°C.

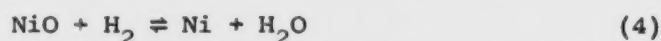
Figure 40. ACTIVATION ENERGY PLOT
GOOD CATALYST VS. BAD CATALYST



The second explanation is that iron oxide, in contrast to the behavior of nickel oxide, was not being reduced under reaction conditions. This can be illustrated by comparing the equilibrium of the Fe-O-H system which is represented by the following three reactions:



With the equilibrium of the Ni-O-H system which is represented by the reaction:



In each of the four equations, the equilibrium constant is of the form $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ where $P_{\text{H}_2\text{O}}$ and P_{H_2} are the partial pressures of water and hydrogen respectively. Figure 41 is an approximate phase diagram for the Fe-O-H system and Figure 42 represents the equilibrium for the Ni-O-H system. These diagrams are derived from consideration of the variation with temperature of the equilibrium constants. The stable phase for any particular condition is determined by location, the correct temperature and partial pressure ratio on the diagram (81).

Table 18 contains the conditions for two experiments, one using mill scale and the other using nickel carbonate as the hydrogenating catalysts. Point A on Figure 41 represents the conditions used during an actual experiment with mill scale as the catalyst as described in the table. Point B, on the other hand, is the point in the reduced region which corresponds to the lowest temperature at which iron will be reduced with the partial pressure ratio found during the experimentation. This reduction occurs at a temperature parameter of 13.7 which corresponds to a temperature of 730°K.

Figure 41. PHASE DIAGRAM FOR Fe-H-O SYSTEM (81)

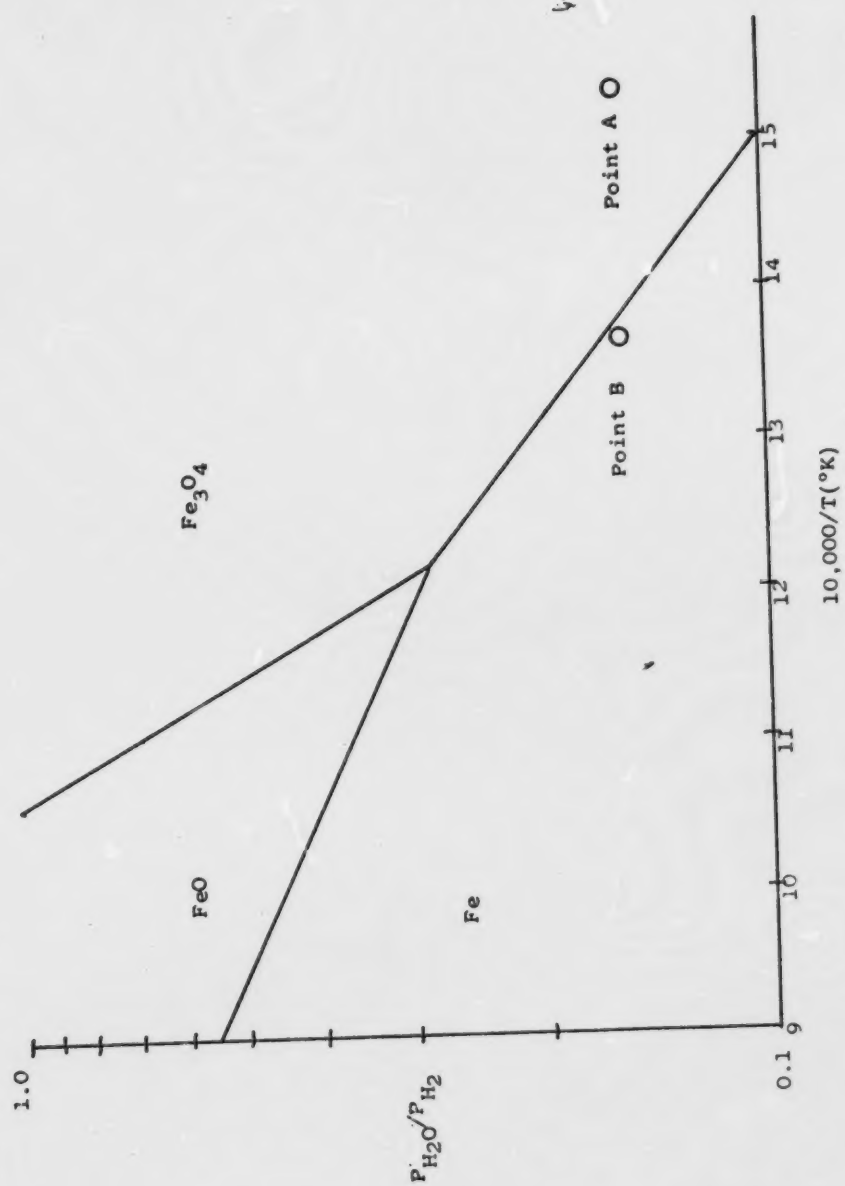


Figure 42. EQUILIBRIUM CONSTANT VS. TEMPERATURE
FOR NiO REDUCTION WITH HYDROGEN (81)

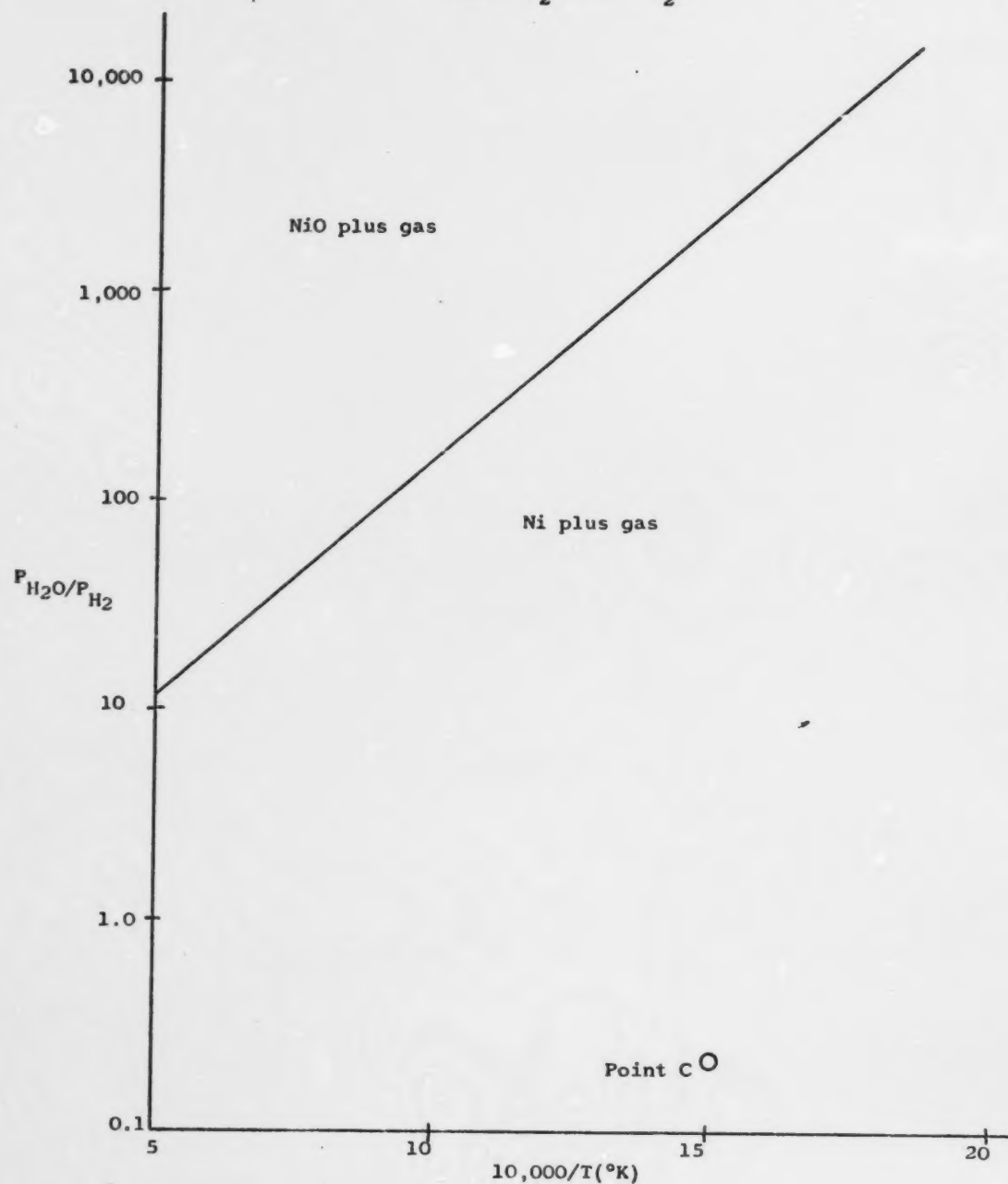
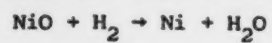


Table 18. CATALYST REDUCTION CONDITIONS

Catalyst	Reaction Temp °C(°K)	Press. at Reac. Temp. atm.	Amount of Water gm	Mol % H ₂ In Prod. gas Dry Basis	P _{H₂O} atm.	P _{H₂} atm	P _{H₂} ^U /P _{H₂}
Millscale	385(659)	90.1	1.0	97.2	12.0	76.3	0.154
Nickel Carbonate	372(645)	68.0	1.0	97.1	11.8	54.6	0.215

Nickel on the other hand was clearly in a reduced state under reaction conditions as evidenced by point C on Figure 42. Point C represents the conditions given for the nickel carbonate catalyst experiment described in Table 16. It is clear that the conditions were not compatible with the presence of reduced iron at the end of an experiment, when 1 gm of water was present.

The catalytic activity of reduced iron cannot, then, be compared to the activity of the other reduced catalysts until tests are performed under conditions which insure that the oxidized states are not favored at anytime during the reaction. This can be accomplished by increasing the hydrogen partial pressure (by charging with more hydrogen initially) and by increasing the reaction temperature, perhaps to 454°C as was described earlier.

Product Oil Quality

The ultimate analysis and heating value of some rocking autoclave products are provided in Table 19. The interpretation of these data is complicated by the hydrocracking of the mineral oil carrier, which proceeded simultaneously. The elemental analyses and heats of combustion were obtained from total oil products (mineral oil carrier and oil made from the solid feed).

Table 19. ULTIMATE ANALYSIS AND HEATING VALUE OF ROCKING AUTOCLAVE PRODUCTS

Feedstock	Product	DAFB	%		%		Severity	Heating value cal/gm	Calc. Heating value cal/gm
Run No.	Sample	Conv. %	Catalyst	Carbon	Hydrogen	Other ^a			
Newspaper	Solid Liquid	61.7	Zeolite Cracking	78.60 ^b 85.73	5.08 ^b 13.87	16.32 0.40	725°F Hold 55 min.	19,200	14,200
Sewage sludge	Liquid	91.6	G-53 Ni	81.83	12.96	5.11	800°F Hold 60 min.	19,730	17,500
Newspaper	Solid Liquid	92.7	G-53 Ni	86.10 ^b 85.69	8.06 ^b 13.72	5.84 0.59	700°F Hold 55 min.	----- 19,490	18,100
Newspaper	Solid Newspaper	62.2	G-53 Ni	73.40 ^b 85.68	5.54 ^b 14.02	22.06 0.30	700°F No Hold	----- 19,700	17,300
Oil Blank	Liquid		G-53 Ni	82.12	13.22	4.66	780° No Hold	-----	-----
Newspaper	Liquid	95.0	G-53 Ni	86.19	13.81	0.00	800° No Hold	19,550	18,500
Powdered Newspaper		---	---	46.50 ^b	5.85	47.65	-----	7,500	-----
Mineral Oil		---	---	85.79	13.92	0.29	-----	19,000	-----

^a By difference

^b Corrected for moisture and ash content

Elemental analyses were performed on both the solid and liquid product samples. The solid samples, in all cases, exhibited a lower oxygen content (6-22%) than the newspaper feed (46%). Most of the liquid samples contained so little "other" in their elemental analysis that the oxygen level could not exceed 5% and in some cases (like the 95% conversion expt.) the value was much closer to zero.

The heats of combustion were determined for the total liquid product. The calculated heating value is the estimated ΔH for the oil arising from the solid feed alone. Both heats of combustion and the elemental analyses indicate the presence of a high quality fuel oil.

EXPERIMENTS ON SEWAGE SLURRIED IN OIL

The Deer Island Sewage Treatment Plant has been servicing a major portion of Boston and surrounding areas since 1968. In addition to coarse and fine screenings and grit removal, the process includes both pre and post chlorination, aeration, sedimentation, sludge thickening and high-rate digestion. The effluent is discharged into the outgoing ocean tides.

There are several pollution problems associated with the operation of this facility. It is estimated that 15-20% of the sludge is redeposited in the harbor.

The high coliform bacteria counts in the area of the plant necessitate restrictions on both the commercial shell fish industry and local recreational facilities. The plant exerts a high Biological Oxygen Demand (BOD) on the inner harbor west of Deer Island.

In light of the difficulties inherent in the disposal of the treated sewage sludge and prior to federal EPA intervention, the Massachusetts Water Resources Commission sponsored a student consulting study starting in the summer of 1971 through the Environmental System Study Program (ESSP) at W.P.I. A five man interdisciplinary team undertook a study on the alternative solutions to ultimate disposal of the Deer Island sewage sludge. A detailed feasibility and cost estimate investigation for three different operations was proposed and accepted for study. These are:

1. Incineration
2. Wet Oxidation
3. Chemical Conversion to Oil

During the summer of 1971 at Deer Island limited experimentation with sludge in a one liter batch autoclave was initiated. During the 1971-1972

school year the ESSP group continued their coordination with the cellulose liquefaction EPA project, working with their sludge as a sample feed stock for testing and experimentation.

The ultimate goals are, first, to test for the optimum catalysts and conditions on a small scale rocking batch autoclave and, second, to operate in the continuous flow stirred tank reactor. In this way, an optimum operational conversion can be established, the product characterized, and the complete system evaluated economically and environmentally.

A representative ten gallon sample of raw sewage sludge, undigested, was transported from the Deer Island Treatment Plant to a cooler at WPI. The sludge was filtered through a centrifugal filter to remove 50% of the water. The 16% sewage concentrate, a pasty filter cake, was dried at 103°C in small evaporating dishes for 12 hours. The dried cakes were broken up and ground to fine particles in a Waring blender. The sludge at this point has relatively little objectionable odor as compared to the undried material. It resembled light weight loose wool. The sludge cannot be ball milled since its grease content caused it to be beaten to a very hard tar.

High pressure studies were performed using the Amino Rocking Autoclave previously described. Samples were heated to 371°C-416°C over a period of 1½ hours. Initial pressures of 68.0 atm, hydrogen, carbon monoxide, or mixtures of both were employed. The autoclave was cooled to 121°C (2 hrs.) and then allowed to return slowly to room temperature.

The autoclave was depressurized and the gases analyzed by gas chromatography as described in the powdered newspaper experiments. The pyrex liner was removed, weighed, and a drop of the liquid was removed for subsequent gas chromatographic analysis. The contents of the liner and

autoclave were filtered using benzene to dilute and wash. The residue was dried, weighed, and the filtrate concentrated using a rotary evaporator.

These experiments (nos. 1-10) showed considerably smaller condensed phase weight losses than those encountered in the powdered newspaper experiments where nickel catalysts were employed. The sludge impurities appear roughly comparable in catalytic activity to the G-53 Nickel on Kieselguhr catalyst. The experiments and their results are summarized in Table 20. They indicate that in the presence of hydrogen and at temperatures in excess of 400°C, sewage sludge is liquefied in high conversion.

A method for determining the per cent composition of cellulose of mixed cellulose and sludge samples was adopted and modified (82). The procedure is that described under the "Gravimetric Determination Method" with the qualification that the muffle furnace is heated gradually from 200°C to 625°C with the samples to prevent immediate ignition and fly ash losses.

Weigh 1 gram of dried ground refuse into a 125 ml flask, add 6 mls water, 25 mls glacial acetic acid, and 2 mls concentrated HNO_3 . Boil gently for 20 minutes, cool to 80°C, and add 50 mls benzene, swirling for about 2 minutes. Decant benzene phase into a Gooch crucible with an asbestos filter or a sintered glass crucible. Add 50 mls of ether to the flask, swirl, and filter. Wash all solids out of the flask with acetone. Wash the filter cake successively with 100 ml portions of hot benzene, hot methanol, and ether. Clean the outside of the crucible and dry at 66°C for 1 hour. Cool in a desiccator and weigh. Place in a muffle furnace at 200°C uncovered, raise the temperature to 625°C, and hold for 1 hour. Cool in a desiccator and weigh.

Pending further tests define

$$\% \text{ cellulose} = \frac{\text{weight loss through ignition at } 625^\circ\text{C}}{\text{original sample weight}}$$

Standardization of the method with pure Solka Floc Wood cellulose

Table 20. SEWAGE SLUDGE AUTOCLAVE EXPERIMENTS

Run	Feed (gm)		Gas (atm)		Heating Duration Min	Max. Temp C	Max. Pressure atm	Final Pressure atm	Recovery condensed solids Phase	% Sludge conversion (DAFB)
	Sludge	Oil	Other	H ₂	CO					
1	---	16.68	---	64.6	---	130	416	128.5	64.6	15.83
2	---	16.20	---	1500	---	100	334	172.0	100.5	ND
3	---	20.60	2.00	66.0	---	90	371	130.0	66.0	20.20
4	3.51	17.74	---	61.2	---	95	385	112.2	61.2	21.24
5	4.61	21.06	---	---	64.0	100	371	119.0	63.9	25.24
6	3.61	18.24	---	39.8	30.6	85	396	128.5	142.6	21.35
7	4.23	21.37	2.33 ^a	62.6	17.0	205(65) ^d	427	171.3	126.8	25.70
8	3.94	25.06	0.200 ^b	59.5	---	110	372	105.3	59.1	29.15
9	3.96	25.34	0.0198 ^b	54.4	---	110	372	98.6	54.1	29.20
10	2.80	17.04	0.141 ^b	47.1	---	130(60) ^d	427	81.9	37.6	18.34 ^c

^aWater^bG-53 Girdler Nickel on Kieselkuhr Catalyst^cElemental Analysis 81.83(C), 12.96(H), ΔH comb 19,730 Btu/lb^dHolding Tmax (min)

were correct to better than one percent. A test determination with a sample of human hair as a protein source established that proteins are dissolved by the acid boiling and not retained as cellulose weight.

Determination of the per cent cellulose in the ground newspaper was 60 to 62%. One determination on the dried ground sludge yielded 32.4%.

Additional standardization tests must be completed including a determination on charcoal before the method can safely be called a "Cellulose" determination and the refuse characterized with accuracy.

LIQUEFACTION OF POLYSTYRENE WASTE

Plastics contribute roughly 2% to the total solid waste production (83). Since considerable regulatory pressure is being applied to the plastics manufacturer, the safe disposal of these materials is of growing concern. Liquefaction studies on a polystyrene industrial waste (a model feed) were conducted at Worcester Polytechnic Institute to determine the feasibility of conversion to liquid fuel oil. The initial results indicate that, at temperatures above 427°C, polystyrene, even in the absence of hydrogen, can be converted to liquid and gaseous products at levels in excess of 95%.

Background

In the thermal degradation process, the polymer undergoes pyrolysis in which the molecular weight drops rapidly during the first five to ten per cent loss of weight then stabilizes at approximately 40,000-60,000. This level is independent of the initial molecular weight of the polymer provided it is greater than the stabilization level. The initial drop is partly due to scissions of weak links in the polymer at branching or due to oxidation of the polymer, but mainly due to thermal scissions in the chain. Degradation continues to the point where the drop in weight

caused by random scissions is counterbalanced by disappearance of smaller chains through unzipping into monomer.

The degradation products from polystyrene are mainly monomers, dimers, and trimers. Fragments break off at free radical chain ends resulting from thermal scissions. Not all scissions result in free radicals—some breaks result in saturated and unsaturated ends due to hydrogen transfer. Those radicals which do form then proceed to remove hydrogen intermolecularly or intramolecularly to cause new scissions.

From polystyrene degradation data (84) it was determined that at temperatures greater than 350°C the polystyrene was 90% degraded. By achieving this high temperature and being able to maintain it for a sufficient period of time, the polystyrene could be converted into aromatic olefin products which would be hydrogenated further in a cellulose liquefaction process. The two experimental tests were a degradation of the polystyrene in mineral oil in a sealed reactor and a distillation of the dry solid waste.

Experiments Using a Carrier Oil

For the experiments using mineral oil as a carrier, the previously described rocking autoclave procedure was used. The feed was obtained by drying a 50-70% water slurry of polystyrene waste (containing 14% ash) at 105°C and then grinding the dried waste to less than 40 mesh. Figure 43 shows a plot of temperature and pressure vs. time and Table 21 shows the experimental results. The liquid products were analyzed using the previously described gas chromatography procedure.

A gas chromatogram of the original mineral oil was also made to determine any changes in its characteristics (see Figures 44-46). From these chromatograms it can be seen that even though the polystyrene was degraded to light oils, the mineral oil was also cracked to lighter ends,

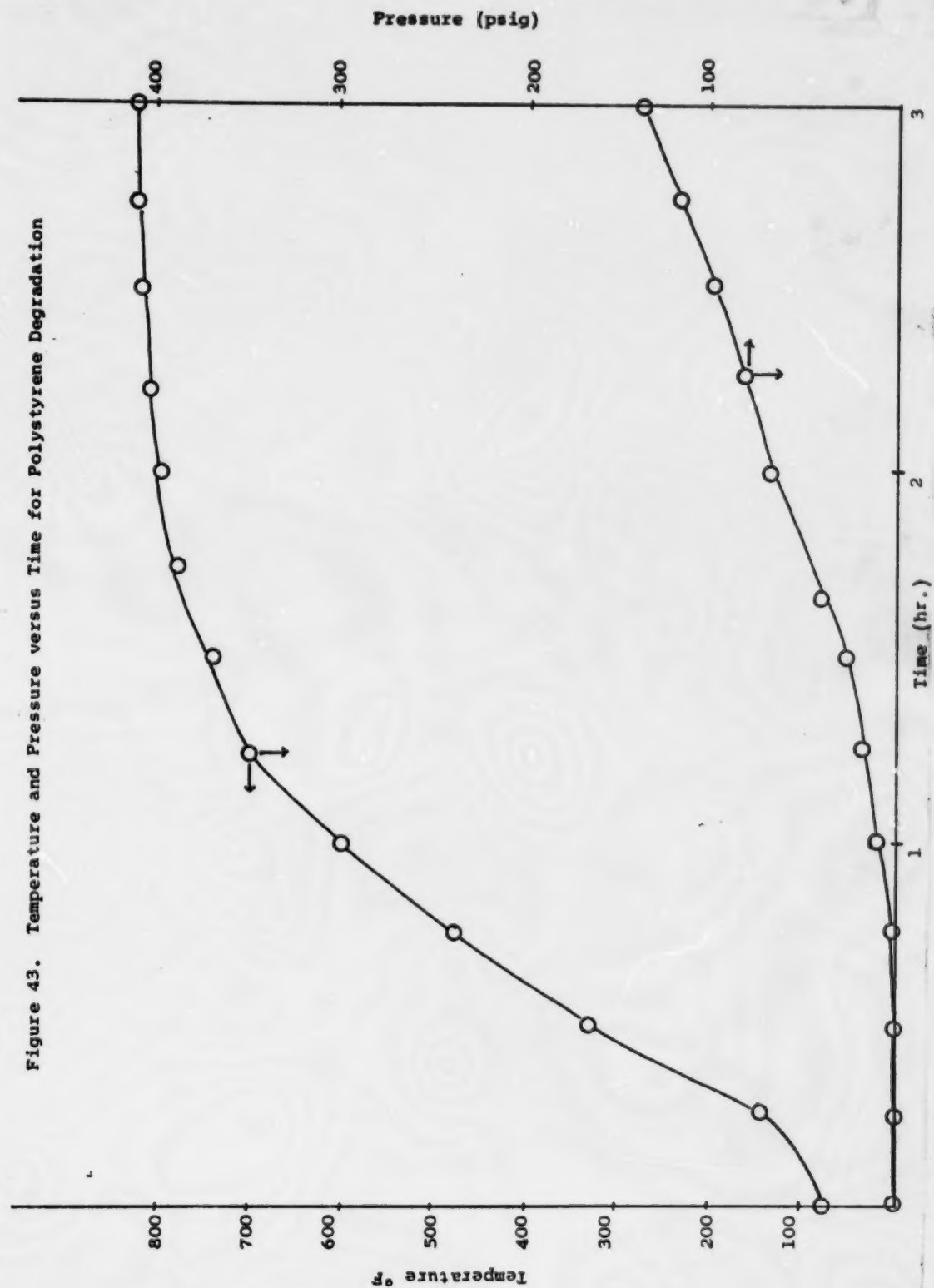


Figure 43. Temperature and Pressure versus Time for Polystyrene Degradation

Table 21. MINERAL OIL AND GROUND DRIED SOLID POLYSTYRENE WASTE RUN

Feed Composition:

Mineral Oil	19.17 g
Ground Dried Solid	<u>6.54 g</u>
Total Feed	25.71 g

Reaction Conditions:

Heat Up	24°-427°C	2 hrs.
Reaction Time	427°-443°C	1.25 "
Cool Down	443-24°C	overnight

Product:

Solid Product	0.62 g
Liquid in Liner	7.28 g
Liquid in Shell	<u>12.19 g</u>
	20.09 g
Weight Loss-Noncondensables	<u>5.62 g</u>
Total Product	25.71 g

Apparent Conversion:

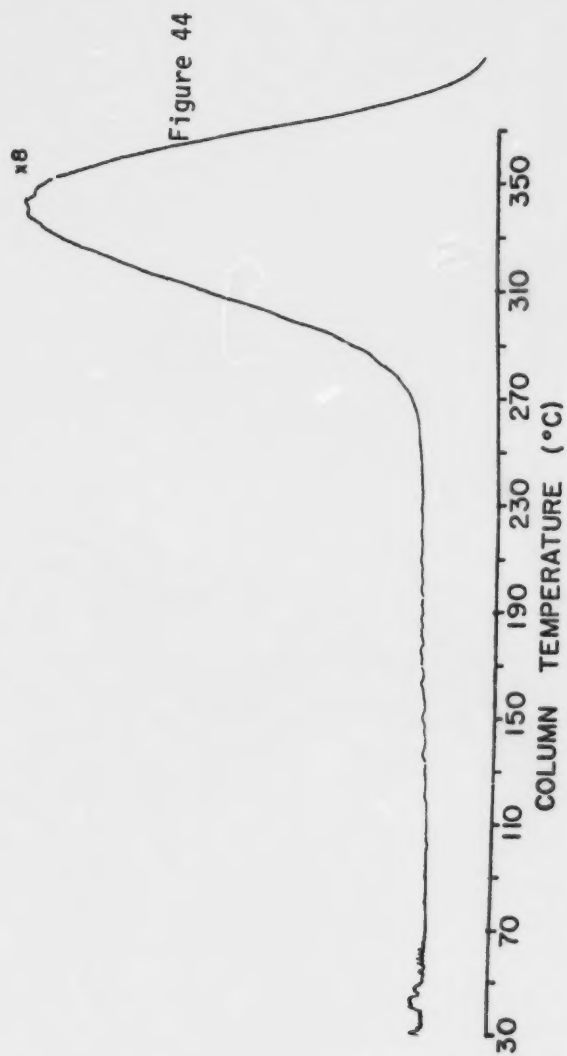
90.5%

Percent Organics in Solid:

50.0%

Actual Organic Conversion:

95.3%



MINERAL OIL USED FOR SLURRY -
BEFORE REACTION (4 μ l)

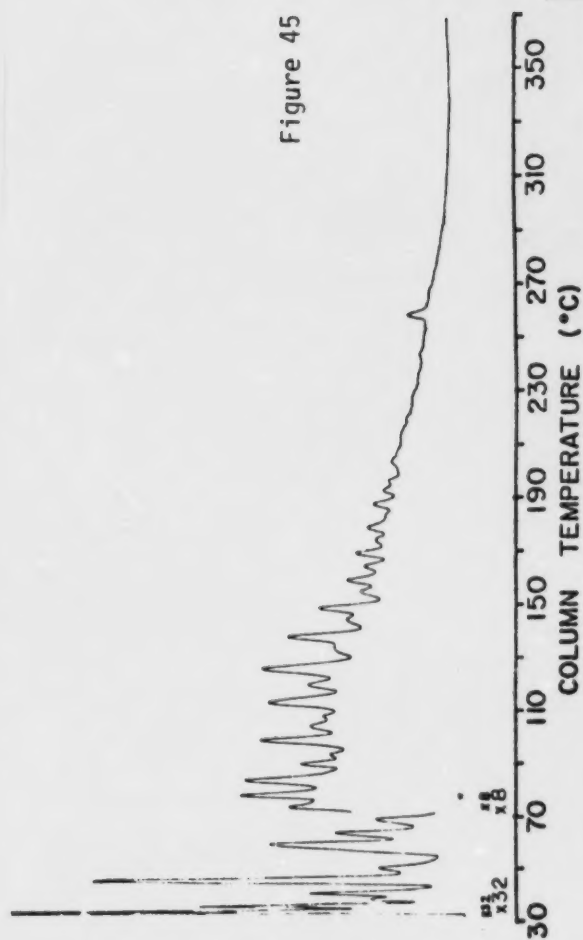
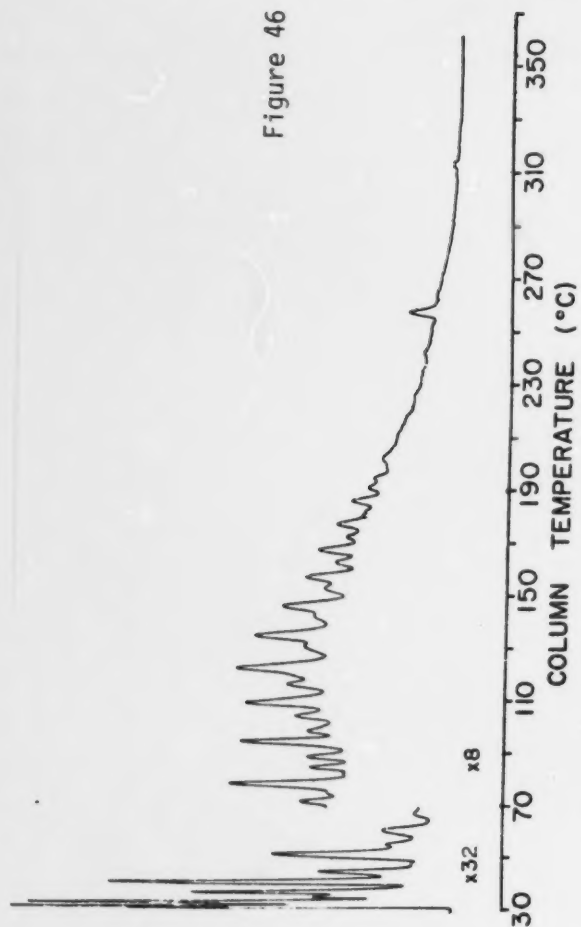


Figure 45

GROUND SOLID AND MINERAL OIL SLURRY
LIQUID PRODUCT FROM SHELL (5 μ l)



GROUND SOLID AND MINERAL OIL SLURRY
LIQUID PRODUCT FROM LINER (5 μ l)

thus making it more difficult to identify the actual polymer degradation products.

For both these and the preceding experiments, the results show that there is no question that polystyrene would be decomposed in the cellulose liquefaction process, since the necessary temperature prevails. In addition, in the liquefaction system, since both nickel catalysts and high pressures of H_2 are present, hydrogenation of the styrenes would proceed.

The solid products were centrifuge separated, washed with acetone, air dried, and weighed: 0.62 g. Apparent conversion was 90.5%. The solids were then analyzed for ash content using ASTM standard procedure designation D 2415-66 (see Table 22). The ash percent of the solid was determined to be 50% thus yielding an actual organic conversion of 95%.

Dry Distillation Experiments

In subsequent experiments, atmospheric distillations of the dried polystyrene waste in chunk form was performed. The autoclave was fitted with a condenser so that volatiles produced could be recovered as a liquid. The glass liner was replaced by an aluminum foil container in the reactor shell. The reactor was heated from room temperature to $454^{\circ}C$ in 2 hours and 15 minutes, then held at this temperature for 4 hours. The entire reaction run was done at atmospheric pressure. After the 4 hours the reactor was cooled to room temperature and disassembled. Table 23 provides the experimental data from these runs.

The liquid condensate was analyzed by gas chromatography. (See Figure 47.) By comparison with the retention times obtained from authentic samples, several of the products were tentatively identified. These results indicated the presence of styrene monomers, dimers, and trimers.

CONDENSATE FROM DISTILLATION OF SOLID POLYSTYRENE
(4 μ l)

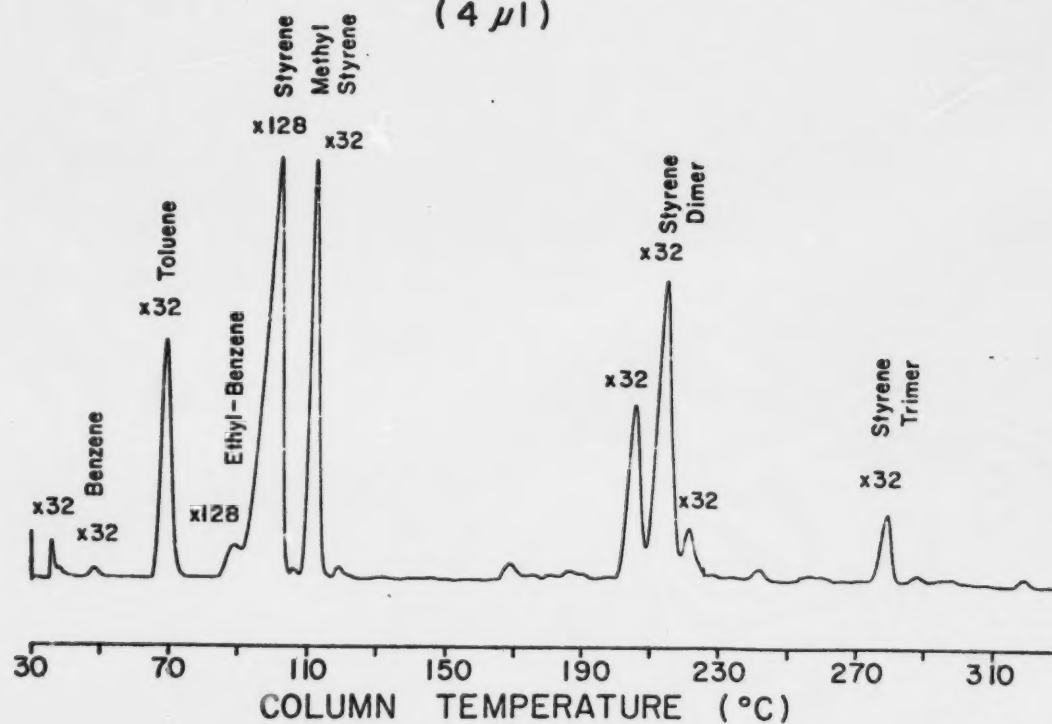


Figure 47

Table 22. PROCEDURE FOR ASH ANALYSIS OF SOLIDS

1. Fire crucible to 900°C.
2. Cool in dessicator and weigh.
3. Add a weighed charge of the sample (mix well to insure uniform composition)
4. Place crucible and sample in cold furnace.
5. Gradually heat sample to 900°C.
6. Remove sample and cool in dessicator.
7. Weigh the crucible.
8. Replace crucible in furnace at 900°C for 30 min.
9. Cool sample and reweigh.
10. Continue until constant weight reached.

Table 23. DRY SOLID WASTE DISTILLATION RUN

<u>Feed:</u>	Run 1	Run 2
Dry Polystyrene Solid Waste	21.08 g	21.03 g
<u>Reaction Conditions:</u>		
Heat Up 24°-454°C	2.25 hrs	
Reaction 454°C	4.0 hrs.	same
Cool Down 454°-24°C	Overnight	
<u>Products:</u>		
Condensate	13.53 g	15.65 g
Liquid Residue	0.72 g	0.39 g
Solid Product	<u>2.13 g</u>	<u>2.22 g</u>
	16.38 g	18.26 g
Weight Loss-Noncondensables	<u>4.70 g</u>	<u>2.77 g</u>
	21.08 g	21.03 g
<u>Apparent Conversion:</u>		
	90%	
<u>Organics in Solids:</u>		
	33%	
<u>Actual Organic Conversion:</u>		
	96.5%	

The solid products were a dry ash found only in the aluminum foil container. This product was removed and weighed: 2.13g. The apparent conversion was determined to be 90%. An ash analysis was done on this solid by the previously mentioned method and the actual conversion of organics was determined to be 96%.

CONTINUOUS PROCESSING STUDIES

LOW SEVERITY PROCESSING OF GLUCOSE IN WATER

Initial studies at low severity conditions were made in the continuous stirred tank reactor (CSTR) unit shown on Figure 48.

Aqueous glucose solutions were pumped under high pressure into the stirred magnesia insulated autoclave by a Lapp Pulsafeeder pump, model LS-30. A liquid flow rate of approximately 750 ml. per hour was fixed at a hydrogen pressure of 100 atmospheres. Liquid and gaseous products were forced out of the autoclave by the high pressure and flowed through a withdrawal line which is equipped with a cooler-condenser. The product was then forced into a Jerguson Gage employed as a high pressure knock out pot. There was a needle valve for adjusting the gas blow-by in the system. This regulated the concentration of gases in the reactor. Finally the products flowed through another needle valve to a low pressure knock out pot where the gases were separated and exited through the top, while the liquid was recovered from the bottom. Gas flow rates into the autoclave were measured by a high pressure Brooks Gas Rotameter. All liquid lines were either 1/8 or 1/4 inch 316 stainless steel tubing, and the gas inlet lines were 1/8 inch copper tubing.

The operating procedure used was as follows:

- 1) Make sure that the autoclave is clean and charge one liter of feed solution through the top. Tighten charge port.
- 2) Next, pressurize the system with nitrogen several times. Check for leaks. Activate stirrer and collect the liquid overflow.

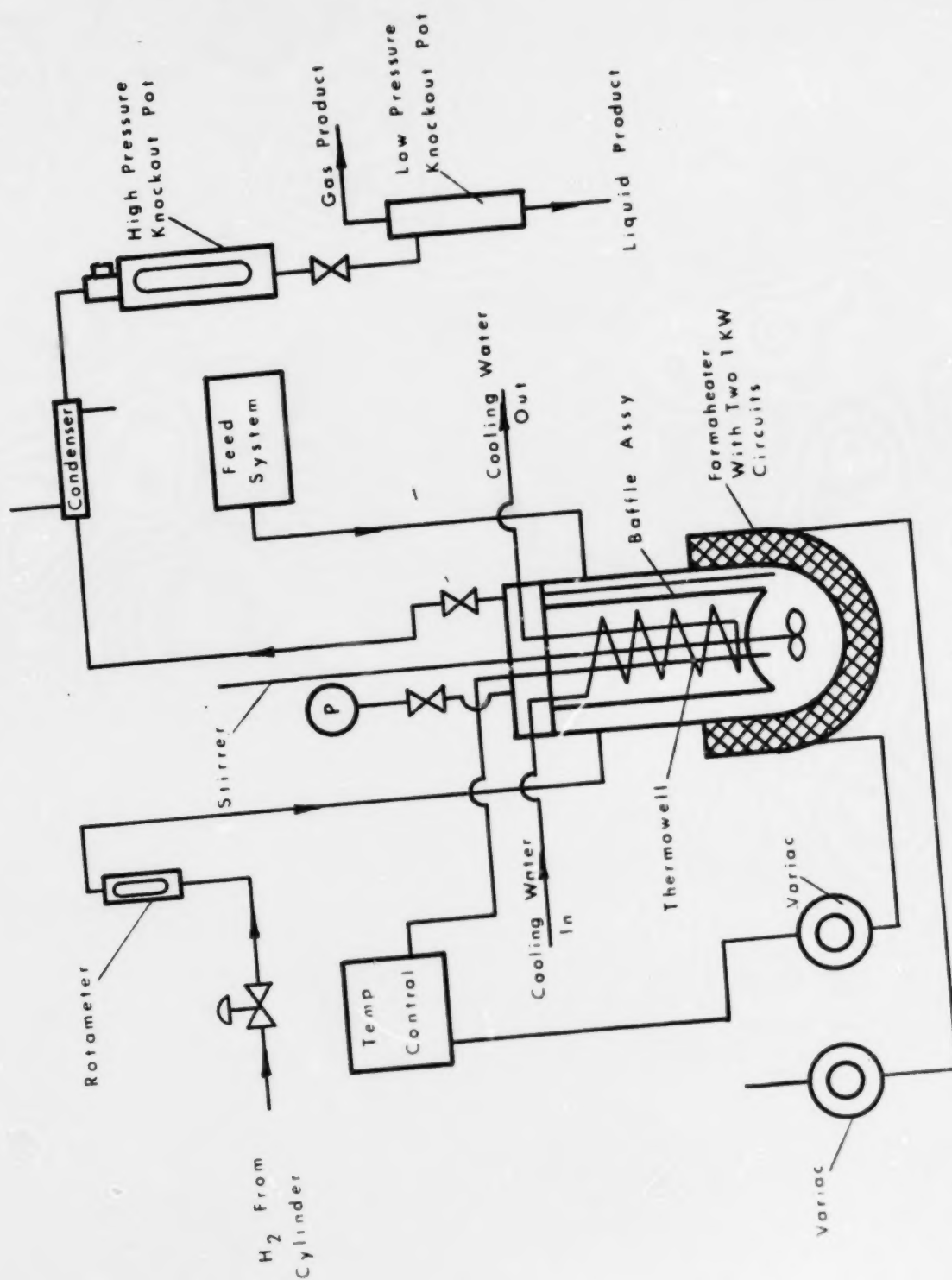


Figure 48

- 3) Switch on the pump and the heating elements. Start water running through the cooler-condenser. Crack the needle valve to allow liquid build up to escape from the autoclave. Use cooling coils as needed.
- 4) Pressurize system with hydrogen several times, and monitor gas flow rates into and out of the autoclave, the pressure, temperature, and time.
- 5) Allow the system to come to steady state and record data.
- 6) Collect and analyze products.

A preliminary run was made to check the equipment under actual operating conditions. Experimental conditions were as follows. A glucose solution of approximately 4500 grams water, 700 grams glucose and 40 grams sodium aluminate was prepared. This solution was pumped at a rate of 750 ml. per hour into the autoclave which held about 720 ml. of solution, giving a residence time of 0.96 hours. Hydrogen gas, at a pressure of 102 atmospheres was introduced and the reactor was heated and stirred. The final temperature reached was approximately 225°C. A gas inlet rate of about 25 cm³ per minute was used.

Samples of liquid product were collected at various intervals. The initial samples were clear but subsequent ones were light brown as the temperature increased. At some later time, the product liquid became dark brown and developed a caramel odor. The condensed phase products started exiting as a foam instead of a liquid. The product eventually lost its caramel odor which was replaced by a phenolic-like odor. This liquid also was discharging finely divided carbon particles, evidence that the later reaction conditions may have been too moderate. Finally, product whose color was black had a burnt odor. The contents of the reactor were

removed and a slight oil slick was present. It should be emphasized that at no time was the system at steady state. The total time of the reaction was between four and five hours.

Subsequent runs were made feeding diesel oil and an aqueous solution of glucose and base (such as sodium carbonate or sodium hydroxide) using two separate Lapp Pulsafeeder pumps. Typically the oil flow rate was approximately 300 gms/hr and the aqueous solution flow rate was about 500 gms/hr with a composition range of 25-35% glucose and 3-7% base. A continuous hydrogen purge with a range of 10-15 SCFH was used. Experimental data for representative runs are listed in Table 24.

The start-up procedure during experimentation was as follows: The flow rate of each feed stream was determined by pumping into a high pressure receiver maintained at the system pressure. The process oil was then circulated through the system at 149 to 204°C and the intended pressure, so that the product lines and receivers would be hot enough to prevent solidification of the tar formed during reaction. After the oil had circulated for at least thirty minutes the aqueous feed was introduced.

In order to obtain accurate results, hourly samples were taken. The liquid and gas flow rates were averaged over this period. Gas samples were taken several times during each hour and analyzed by gas chromatography. Shut down was accomplished by stopping the aqueous feed and allowing the system to operate with oil for at least one hour. After this, cooling water was used to cool the reactor which was then vented to atmospheric pressure. A blank run was made using the process oil alone (i.e., no aqueous solution) and hydrogen at 316°C and 102 atm. It was found that hydrogen had no effect on the process oil.

The reaction products at this mild temperature were composed of

Table 24. LOW SEVERITY EXPERIMENTS USING GLUCOSE SOLUTIONS

Run Number	EO72271	EO72671	EO80271
Time on stream (hours)	3	4.5	7
Reaction temp.	316°C	316°C	316°C
Reaction Pressure	102 atm	100 atm	100 atm
Glucose cons. (in) in aq. feed	33 wt %	33 wt %	30 wt %
Glucose conc. (out) in aq. feed	nil	nil	nil
Base used	Na ₂ CO ₃	Na ₂ CO ₃	Na ₂ CO ₃
Base conc. in (Kg of base/Kg of glucose	0.11	0.11	0.085
Base conc. out (Kg of base /Kg of glucose	nil	nil	nil
Feed rate (aq.)	510 gms/hr	510 gms/hr	400 gms/hr.
Feed rate (oil)	310 gms/hr	310 gms/hr	320 gm/hr
Gas flow rate (in)	15 cuft/hr	15 cuft/hr	10.3 cuft/hr
Feed pH	9.65	9.4	9.5
Reaction pH	3.6	3.95	3.1
Density - Feed	0.89	0.89	0.933
Density - Product	0.875	0.84	0.936

- 1) a viscous black material that solidified on standing
- 2) a dark brown organic liquid, and
- 3) a light yellow aqueous liquid.

The viscous black material melted over a broad range (100-200°C) and was soluble in polar organic solvents (acetone, ethanol). The infrared analysis (CHCl_3) of this tar showed it to be aliphatic, with both hydroxy and carbonyl chromophores. Unsaturation of the carbon skeleton was also noted.

The proximate analysis of this black solid is shown in Table 25 along with some typical analyses for solid wastes and its pyrolysis residue.

The product gas was shown to contain hydrogen, the major component, along with traces of CO , CO_2 , and CH_4 .

Samples of the liquid phase products, both organic and aqueous, were derivatized (TMS) and analyzed by gas chromatography. No glucose was detected. The organic phase was composed of the diesel fuel carrier oil, which was shown by glc to be unchanged during the reaction. Two liters of the aqueous phase were extracted continuously with ether for 72 hrs. and shown to contain relatively large quantities (25-35 ml/liter) of ether soluble materials.

Table 25. PROXIMATE ANALYSIS OF FEEDS AND PRODUCT TAR

	Product Tar		Raw Municipal ⁷⁶ Refuse		Pyrolysis ⁷⁶ residue 500-900°C
	as received	dry	as received	dry	
Moisture	15.9	----	43	----	2.6
Volatiles	53.6	63.8	43.0	76.3	4.4
Fixed carbon	24.4	29.1	6.7	11.7	29.6
Ash	<u>5.9</u> 99.8	<u>7.0</u> 99.9	<u>7.0</u> 100.0	<u>12.0</u> 100.0	<u>66.0</u> 102.6

Gas chromatographic analysis of the gaseous products from the reactor utilized two different columns, a molecular sieve 13X using N_2 as the carrier gas for hydrogen and methane and Porapak Q-S using He as the carrier gas for CO , CO_2 , H_2O and methane.

The results of this study show the need to operate at temperatures high enough that a reaction severity suitable to pass the tar-acid stage is developed. Product pH's of 3.1 to 3.95 indicate that this was not the case in this work. Since higher temperatures in the presence of liquid water would require inordinate (and uneconomic) pressures, it is possible to reach a conclusion that the low severity process has no merit for making liquid fuel. Hydrogenation did not occur.

HIGH SEVERITY EXPERIMENTS WITH POWDERED NEWSPAPER

THE PROCESSING SYSTEM

A low vapor pressure white mineral oil carrier was used to transport a hydrogenation catalyst and organic reactants to a continuously stirred tank reactor (CSTR) operating at 60-100 atm. pressure and 432°C to 455°C (see Figure 7). The use of this oil carrier permits operation temperatures that are not limited by the critical temperature of water. (The oil specifications were given in Table 12). The higher temperatures aid the nickel hydrogenation catalyst in effecting nearly complete oxygen removal.

Hydrogen gas strips the oxygen from the cellulosic molecules. A fraction of the hydrogen is generated in-situ by the water gas shift reaction over the nickel hydroxide catalyst employed in the process.

PROCEDURE SUMMARY

Hydrogen gas was loaded by a compressor from shipping to storage cylinders at 235 atm. and passed at a controlled rate into the CSTR, a one liter Autoclave Engineers Model AFP-1005 magnetically stirred stainless steel autoclave with a controlled heating jacket.

Reaction in the CSTR proceeds at final product conditions. Because of this, transition through plastic stages, as in a batch or tubular reactor, is avoided.

The one-liter CSTR was operated using twenty percent by weight powdered newspaper slurries in mineral oil. The powdered newspaper was prepared by first grinding newspaper in a hammer mill and then ball milling. The use of finely powdered newspaper at the pilot level avoided clogging and blocking of valves and lines. In this way, the reaction was studied in the absence of many of the transport phenomena that control

for larger size particles. It should be noted that particle size is a very important economic factor. In a practical process, designing for fine powder will be neither practical nor economic.

The hydrogenation catalyst employed was nickel hydroxide. It was prepared as has been described previously in the section on catalyst screening. Catalyst loading amounted to 0.2 wt. % based on the weight of carrier oil.

Typical reaction conditions for the CSTR pilot unit are summarized below:

Newspaper in Carrier Oil	20 wt. %
Reactor Temperature	400°C - 463°C
Reactor Pressure	34 - 102 atm.
LHSV	1.5 - 4
Residence Time	15 - 38 minutes
Residence Time Ni(OH) ₂ Catalyst (based on newspaper)	0.2 wt. %

The products pass through an air cooled line and are cooled to about 175°C for separation in a 35 cc Jergeson Gage. Liquids and solids are withdrawn by a level control system, and hot gas is reduced to atmospheric pressure through a Mity-Mite regulator, which controls the reactor pressure in the range of 34 atm. Atmospheric flash and vent gases are combined, condensibles separated, and "dry" gas is passed through an analysis train of infrared detectors and a gas chromatograph. I.R. detection of carbon monoxide and carbon dioxide content of the product gas provides the indication of steady state operation in the system.

Gaseous products were analyzed by gas chromatography using a Carbo-sieve-B column (see Table 26 for a typical analysis). Gas samples from other CSTR runs were investigated using the interfaced GC-MS technique for unequivocal identification of components (see Table 27). Both ultimate and proximate (85) analyses were made on the solid products. Material balances over the system, based on the amount of process oil in, were within $\pm 3\%$ accuracy. Carbon conversion ranged from 40-80% while net oil yield varied from 5.2 to 46.1 grams per 100 grams newspaper fed.

Water produced in this system is contaminated by organic products and would need treatment in an ultimate process before disposal (86,87). The water has a dark brown color and an unpleasant phenolic odor. Percolation through activated carbon columns was found to be an effective method for water purification. After treatment, the water was colorless and odorless. Its pH rose from 3 to 5.

RESULTS

The results of the CSTR experiments charging powdered newspaper slurried in paraffin oil are summarized in Table 28. This table lists both blank runs and those with newspaper feed. Reaction conditions, material balances, net oil yields, and percent carbon conversions are presented. Table 29 lists elemental analyses (carbon, hydrogen, oxygen) for solid and liquid samples taken from the CSTR runs. It is from these values that the percent carbon conversions listed in Table 28 are calculated

$$\% \text{ C Conv.} = \frac{(\text{Gm. C in Paper Feed}) - (\text{Gm. C in Solid Product})}{(\text{Gm. C in Paper Feed})} \times 100$$

In the future, the work-up of the data will be facilitated by the use of four recent specifically designed computer programs which will aid in the CSTR and gas chromatography calculations.

Table 26. CSTR PRODUCT GAS COMPOSITION^a

Species	Mole %	Weight %
H ₂	76.80	11.60
CO ₂	3.73	12.40
CO	2.28	4.80
CH ₄	2.54	3.07
C-2	1.31	3.00
C-3	1.75	5.83
C-4	3.20	14.02
C-5	8.34	45.28

^aReaction Conditions: 45°C; 63.2 atm., 1.92 LHSV; 19.8 wt. % Newspaper feed in Mineral Oil; 74.3% Carbon Conversion; 24.4 gms. oil produced per 100 gms. newspaper fed. 10.9 gms. H₂ fed/100 gms. newspaper fed

Table 27. RELATIVE COMPOSITION OF HYDROCARBON GASES

CSTR Run No. DG072572

Peak	% by Wt.	Identity
1	12.7	Methane + (CO) ^a
2	12.1	Ethane, Ethylene + (CO ₂) ^a
3	12.4	Propane
4	6.7	Propene
5	2.0	Iso-butane
6	10.2	n-butane
7	2.9	1-butane
8	3.1	Iso-butene
9	2.1	trans-2-butene
10	1.4	cis-2-butene
11	3.7	Iso-pentane
12	5.7	n-pentane
13	3.4	2-Me-1-butene
14	1.7	1-pentene
15	2.2	cis&trans 2-pentene
16	2.2	2-Me-(1 or 2) butene C ₆ H ₁₄ +C ₅ H ₁₀
17	3.0	Hexane + C ₆ H ₁₂
18	3.4	1-hexene
19	1.3	2 or 3-hexene
20	0.5	2-Me-2-pentene
21	0.9	C ₇ H ₁₆
22	0.8	C ₇ H ₁₄
23	1.6	Unknown
24,25,26	4.1	Unknown

^adetected by mass spectrometer

Table 28

EXPERIMENTAL RESULTS FROM CSTR PILOT PLANT

Weight Percent of Carrier Oil Charged										MAT. ^a		WT% CARBON CONV	OIL YIELD WT% NSPR ^b			
TEMP °C	PRES ATM	SPACE TIME MIN	Ni(OH) ₂ CAT. IN	WATER IN	H ₂ IN	TOTAL IN	PROD OIL OUT	SOLIDS OUT	CO	CASES PRODUCED CO ₂	CH ₄			C ₂ -C ₄	H ₂ OUT	TOTAL OUT
BLANK RUNS - 100g CARRIER OIL WITH CATALYST (NO NEWSPAPER)																
454	58.5	43.7	1.6	-	10.1	111.7	91.8	-	-	-	0.7	5.84	-	10.4	108.7	2.59
421	59.9	43.7	1.6	-	-	-	92.6	-	-	-	-	-	-	-	-	-
371	62.5	43.7	1.6	-	-	-	91.7	-	-	-	-	-	-	-	-	-
EXPERIMENTS WITH 22.3 GRAMS NEWSPAPER ^b PER 100 GRAMS CARRIER OIL																
463	73.8	38.5	-	-	6.46	130.6	106.6	3.66	1.17	1.62	0.588	4.167	6.99	5.64	130.3	0.23
452	70.8	15.1	-	-	2.72	126.9	110.3	4.32	2.2	1.58	0.024	1.686	2.86	1.54	124.5	1.90
401	67.0	15.1	0.05	1.80	2.92	127.1	107.2	9.10	1.06	2.02	0.107	0.868	3.98	2.27	126.6	0.19
454	63.2	31.3	-	-	5.56	129.7	105.5	4.76	2.5	2.84	1.31	6.385	4.64	4.47	132.4	-2.08
454	55.7	20.0	-	-	2.90	127.0	101.2	5.34	0.97	10.8	0.368	2.558	6.76	1.48	129.4	-1.89
EFFECT OF 0.45 GRAMS Ca(OH) ₂ ADDED TO 22.5 GRAMS NEWSPAPER PER 100 GRAMS CARRIER OIL																
454	64.0	31.3	0.05	1.80	2.45	127.1	106.4	8.05	0.69	1.79	0.251	3.484	5.51	1.69	127.9	-0.63
																49.3
																28.4

a. (IN-OUT/IN) x 100

b. Dry Basis - Actual Newspaper Contains Approximately 8% Moisture

Table 29. ELEMENTAL ANALYSIS OF FEEDS AND PRODUCTS FROM C.S.T.R. EXPERIMENTS

<u>Reaction Conditions</u>					
Temp °C	454	463	452	401	454
Pressure (ATM)	58.5	70.8	70.8	67.0	36.7
Space Time (min)	43.7	38.5	15.1	15.1	20.0
					31.3
					64.0
					31.3
<u>Element Wt. %</u>					
	<u>Mineral Oil Feed</u>		<u>Liquid Products</u>		
Carbon	85.79	85.68	86.00	85.86	86.44
Hydrogen	13.92	14.23	13.59	13.89	13.11
Other ^a	0.29	0.09	0.41	0.25	0.45
H/C Ratio	1.91	1.97	1.89	1.94	1.82
					1.85
					1.88
					86.28
					13.51
					0.21
					1.88
<u>Element Wt. %</u>					
	<u>Newspaper Feed</u>		<u>Solid Products</u>		
Carbon	45.36	--	58.52	65.11	54.76
Hydrogen	5.71	--	4.75	6.22	4.44
Oxygen	39.28	--	19.80	7.79	20.79
Other ^a	9.65	--	16.93	20.88	20.01
					11.76
					64.32
					4.09
					11.30
					20.29

^aBy Difference

Based on these investigations, it is possible to draw preliminary conclusions about the effects of temperature, pressure, space time, and calcium hydroxide on the conversion of newspaper to liquid fuel oil.

Effects of Temperature - When the reaction temperature was lowered from 452°C to 401°C (at 69 ± 2 atm. and 15.1 minutes space time) the percent carbon converted and net oil yield (wt. % newspaper) were both reduced: 74.1% and 46.1% versus 38.5% and 32.0%, respectively. The hydrogen consumption decreased from 1.18 grams to 0.65 grams per 100 grams carrier oil fed. The production of hydrocarbon gases also fell.

The bituminous material that is shown in Figure 49 was obtained after inspection of a CSTR following an experiment with powdered newspaper in paraffin oil. It is similar in appearance to the bitumen observed in the previously mentioned low severity glucose experiments.

Effects of Pressure - There was an increase in the net oil yield from 5.2 to 46.1% when reaction pressure was increased from 36.7 atm. to 70.8 atm. (453°C and 17.5 ± 2 minutes space time). The percent carbon converted remained practically constant (69.4% vs. 74.1%).

Effects of Space Time - Figure 50 shows plots of carbon conversion and oil and gas yields versus space time at almost constant conditions of 452-463°C, 63-71 atm. Oil yield passed through a maximum approaching limit of 55 wt. % (based on stoichiometric conversion of carbon to hexane). The percent carbon converted increased rapidly and then leveled off. Ultimately, one would expect the decrease in oil yield from 46.1% to 29.3%. The amount of water produced increased from 1.18 grams to 5.19 grams (per 100 grams of carrier oil fed). The percent carbon converted was 74.1% and 78.6%, respectively. The increased severity (as space time) results in greater oxygen stripping at the expense of volumetric oil yield.



Bituminous Material from a CTSR Run

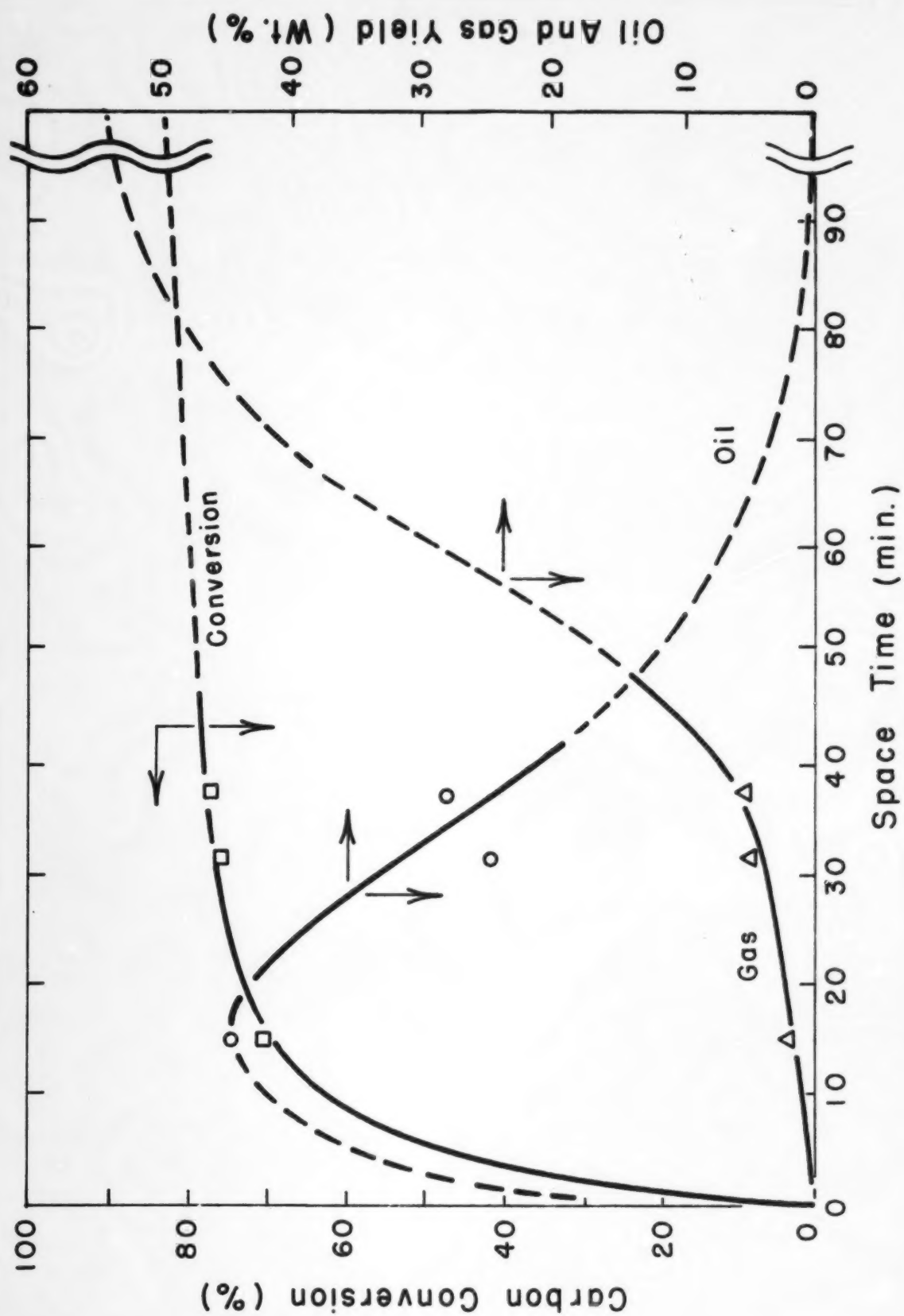


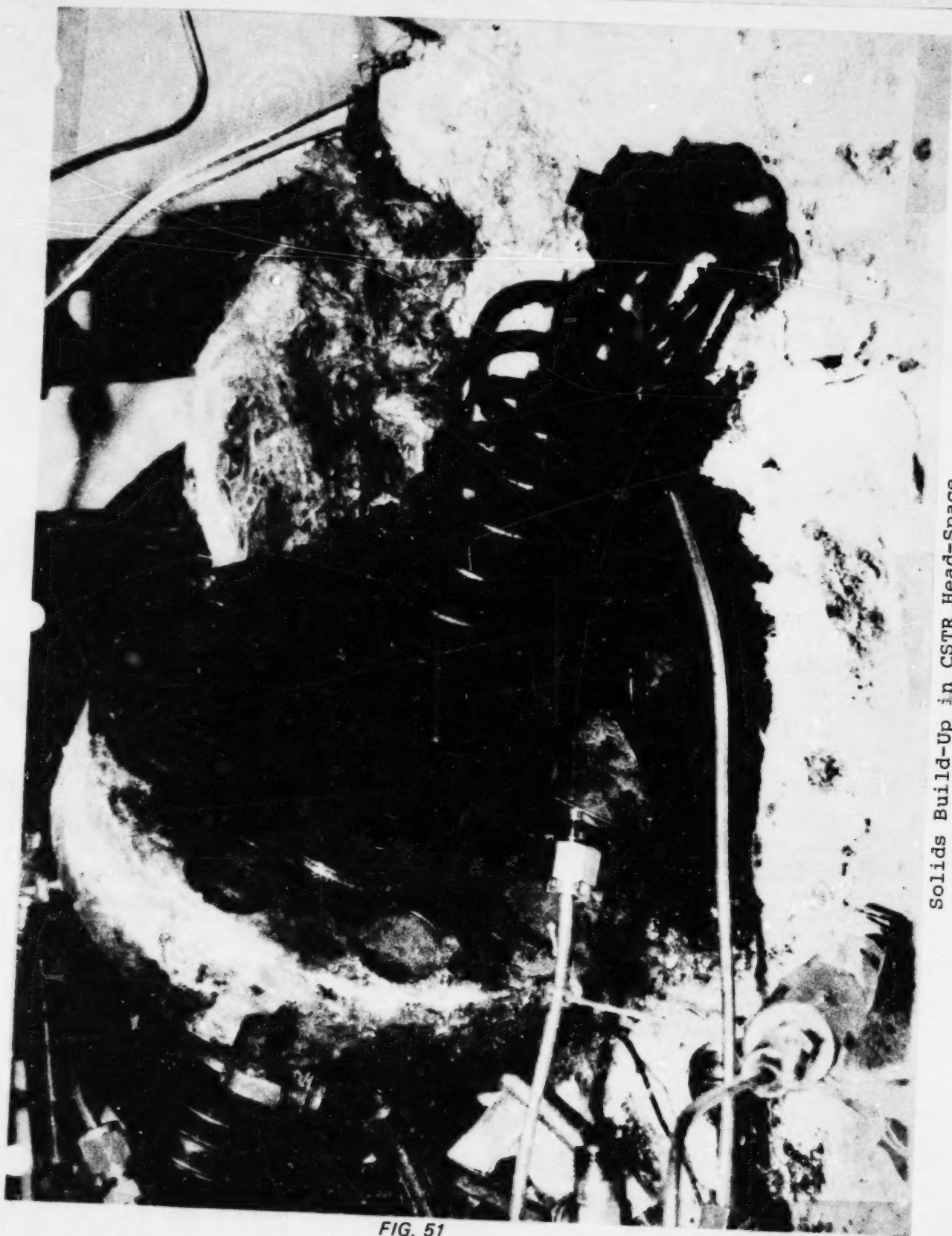
Figure 50

Effects of Calcium Hydroxide - At 454°C, 63.5 atm., and 31.3 minutes space time, the addition of calcium hydroxide reduced the amount of gasification from 11.95 to 5.45 grams per 100 grams carrier oil fed. The carbon converted decreased from 74.3 to 49.3% while the net oil yield increased from 24.4 to 28.4%. When calcium hydroxide was added, a greater proportion of the newspaper was converted to oil and less to gases.

ROLE OF OIL

The CSTR system was operated originally with a 300 ml. head space in the one-liter reactor. As a result, solid char accumulated on the stirrer shaft and cooling coils in this region. Figure 51 shows the solids build-up in the reactor head space. The head space was eliminated in subsequent operation. It is this build-up that has led to the conclusion that the oil is necessary for the reaction to proceed. It is suspected that the cellulose decompose at the high temperatures to oil soluble fragments which migrate to the catalyst in the slurry for hydrogenation. If so, the oil functions not only as a transport and reaction medium for the solids but also serves a key role in the reaction.

In the pilot plant work, a certain amount of hydro-cracking of the paraffinic carrier oil occurred. This is seen in Figure 52, which compared boiling point chromatograms of oil from hydrogenated mineral oil plus newspaper and of hydrogenated mineral oil with that of the unreacted mineral oil. This hydrocracking produces a very small amount of hydrogen. It is believed that used lubricating oils, crude oils, or usual hydrofining feeds not only could serve as carrier oils, but would also be cleaned up in the solid waste conversion process. Such single pass processing could be an alternative to recycling product oil. If dry waste was fed directly to the reactor through a pressure lock system, almost no recycle oil would be needed.

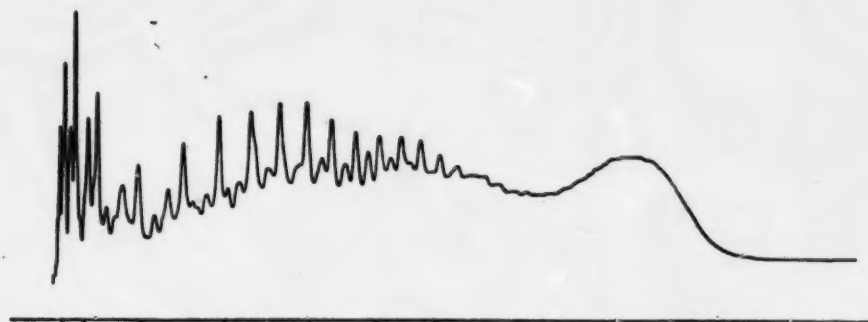


Solids Build-Up in CSTR Head-Space

Figure 52

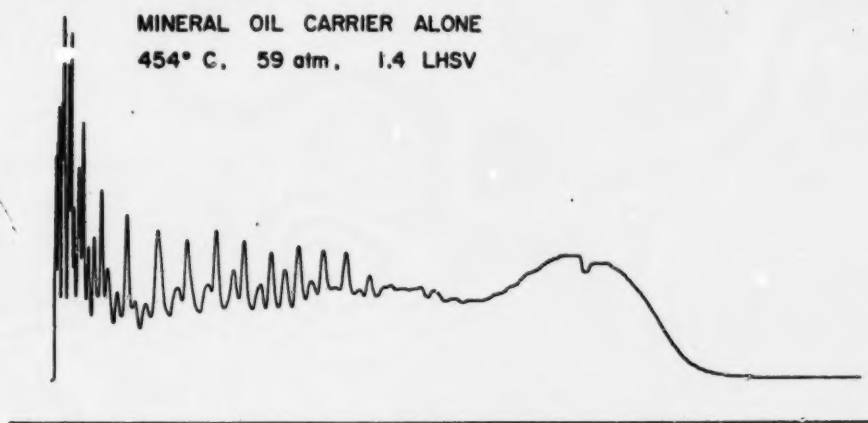
NEWSPAPER + MINERAL OIL CARRIER

463° C. 71 atm. 1.6 LHSV

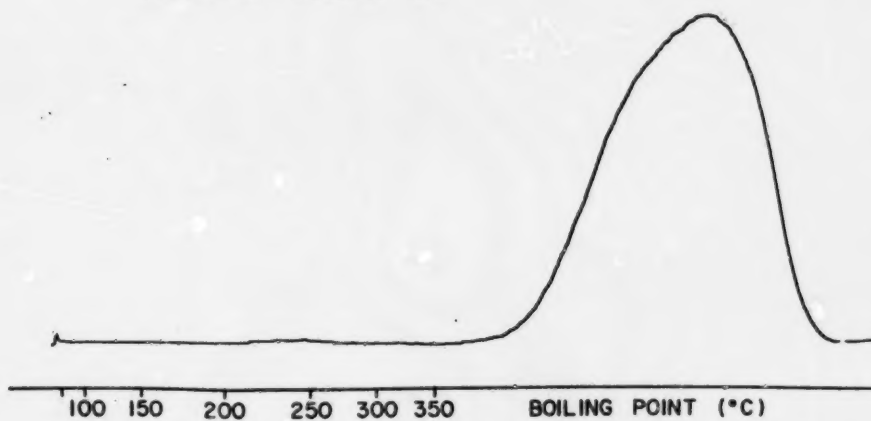


MINERAL OIL CARRIER ALONE

454° C. 59 atm. 1.4 LHSV

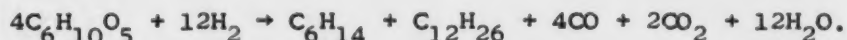


UNREACTED MINERAL OIL

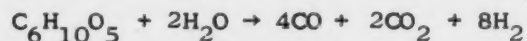


WATER GAS SHIFT REACTION

Material balances suggest that a crude approximation of the stoichiometry is:



The purpose of the above equation is informative. The glucose formula is used to model solid waste, and the six- and twelve-carbon hydrocarbon products represent low and high boiling product components. (But, by no means, pure hexane and dodecane). The importance of the stoichiometry is that it shows CO and CO₂ formation proceeding in-situ by the water gas shift reaction



at a level of about 50% of the hydrogen requirements. Note that when part of the cellulose is converted to hydrogen in this manner, an oil production of 0.324 cu. meters/metric ton dry organic solid waste can be expected.

PROCESS SCALE-UP

Organic material that is not converted in a single pass operation will be recycled almost to extinction in a practical process. Also, an ultimate process would not use mineral oil as a carrier. Rather, a fraction of the oil produced from the solid waste would be recycled as carrier. For example, in a commercial operation using 25 wt.% organic solids in oil, the recycle stream would be three times the weight of the fresh feed. The product oil from a single pass conversion of 85 wt.% will correspond to a product oil produced from solid waste at 95 wt. % conversion using a 3:1 recycle ratio. Figure 53 is an overall material balance block diagram for a commercial system to process 1000 metric tons of solid waste organics per day.

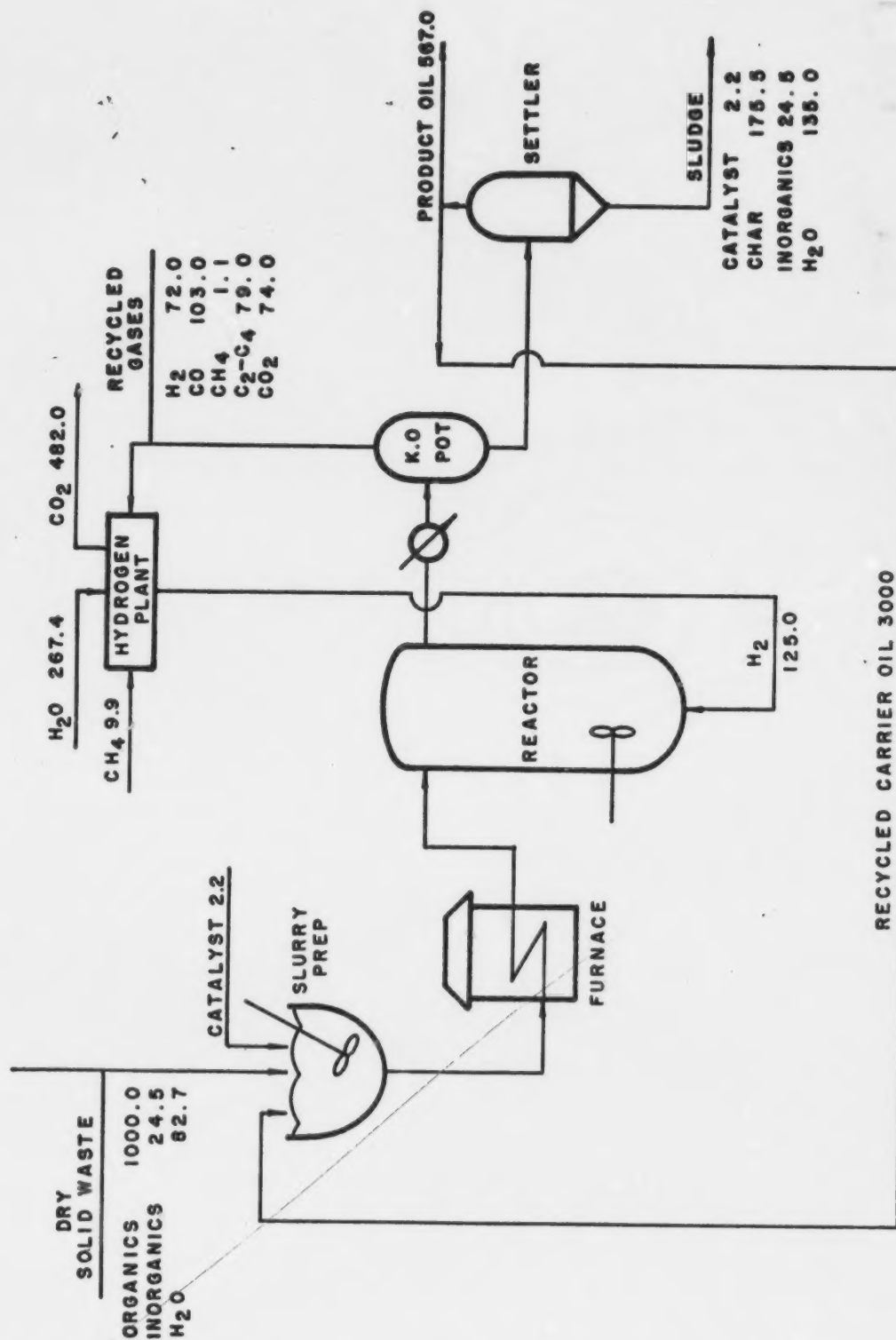


Figure 53

The limited and preliminary pilot plant studies have established that it is technically feasible to hydrogenate cellulosics to fuel oil. Process optimization studies directed towards scaling the pilot plant to an actual commercial demonstration unit to produce oil from municipal solid waste are required before the process can be applied.

HOLDEN DESIGN STUDY

INTRODUCTION

The solid waste problem faced by the United States is a rapidly increasing refuse production coupled with inadequate means of disposal and/or reuse of refuse produced. Presently, the most useful methods of solid waste management are landfill and incineration - dissipative processes that recover no values from solid waste. Methods such as composting, compaction, pyrolysis and steam generation are used to a limited extent and permit some resource recovery.

The solid waste liquefaction process provides a solution to both major problem areas by using organic solid wastes as a raw material to produce a high energy, low sulfur hydrocarbon oil to be used as either fuel oil or refinery feedstock. The design study which follows is a preliminary attempt to understand the intricacies of scaling up the cellulose liquefaction process to a 36 ton per day (TPD) pilot plant capable of processing all organic wastes for the town of Holden, Massachusetts. This small plant would then serve as a pilot plant to develop and optimize the process so that, e.g., a 1000 ton/day plant might next be built.

TOWN OF HOLDEN

General

The town of Holden, Massachusetts is located near the middle of Worcester County and about seven miles northwest of the City of Worcester. It is bordered on the southeast by Worcester, on the west by Paxton, on the northwest by Rutland and Princeton, and on the east by Sterling and West Boylston. The population of the town is given as 12,500 in the last census (1970).

According to data received from the Town Manager, the present (1972) solid waste production of the town amounts to 12,500 tons/year of which 15% (or 1875 tons/year) is garbage and 25% (or 3120 tons/year) is non-combustibles (metals, glass, etc.).

Growth Trends

Figure 54 represents the population growth of the Town of Holden over the years 1920 to present. Since about 1950 the population of the town has been growing rapidly, and all indications are that it will continue to do so in the future. The dotted portion of the curve represents the projected increase of population during the period 1970-1990.

As a result of the population growth of Holden, and the general trend in the United States for more disposable packings, etc., the refuse production of the town is also expected to grow. Figure 55 shows the results of two studies made to project the increase in refuse production that the town will face in the future. By 1990 the amount of refuse generated by the town will be approximately double present amounts.

Refuse Disposal System

At present, two separate means of disposal of refuse are employed by the town. First, garbage is collected from the residents by a contractor who takes it to a pig farm in a neighboring town. Second, the remaining refuse (combustibles and non-combustibles) is disposed of in the town's River Street Sanitary Landfill facility.

The town employs no municipal refuse collection system. Other than garbage, which is collected by the contractor previously mentioned, the residents are responsible for bringing their refuse to the landfill site. A few private collection agencies have emerged and residents may use this means of collection.

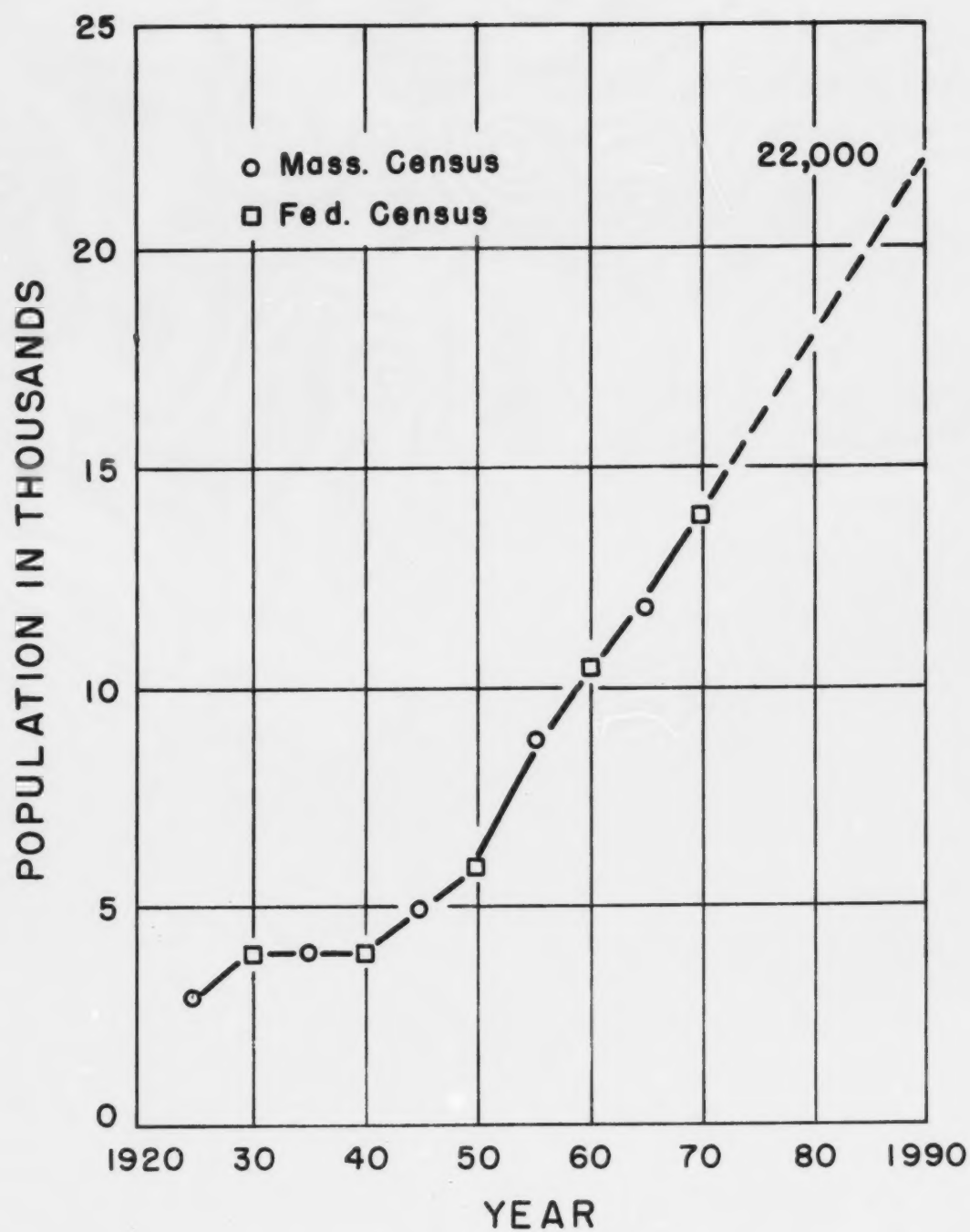


Figure 54

ANNUAL REFUSE PRODUCTION

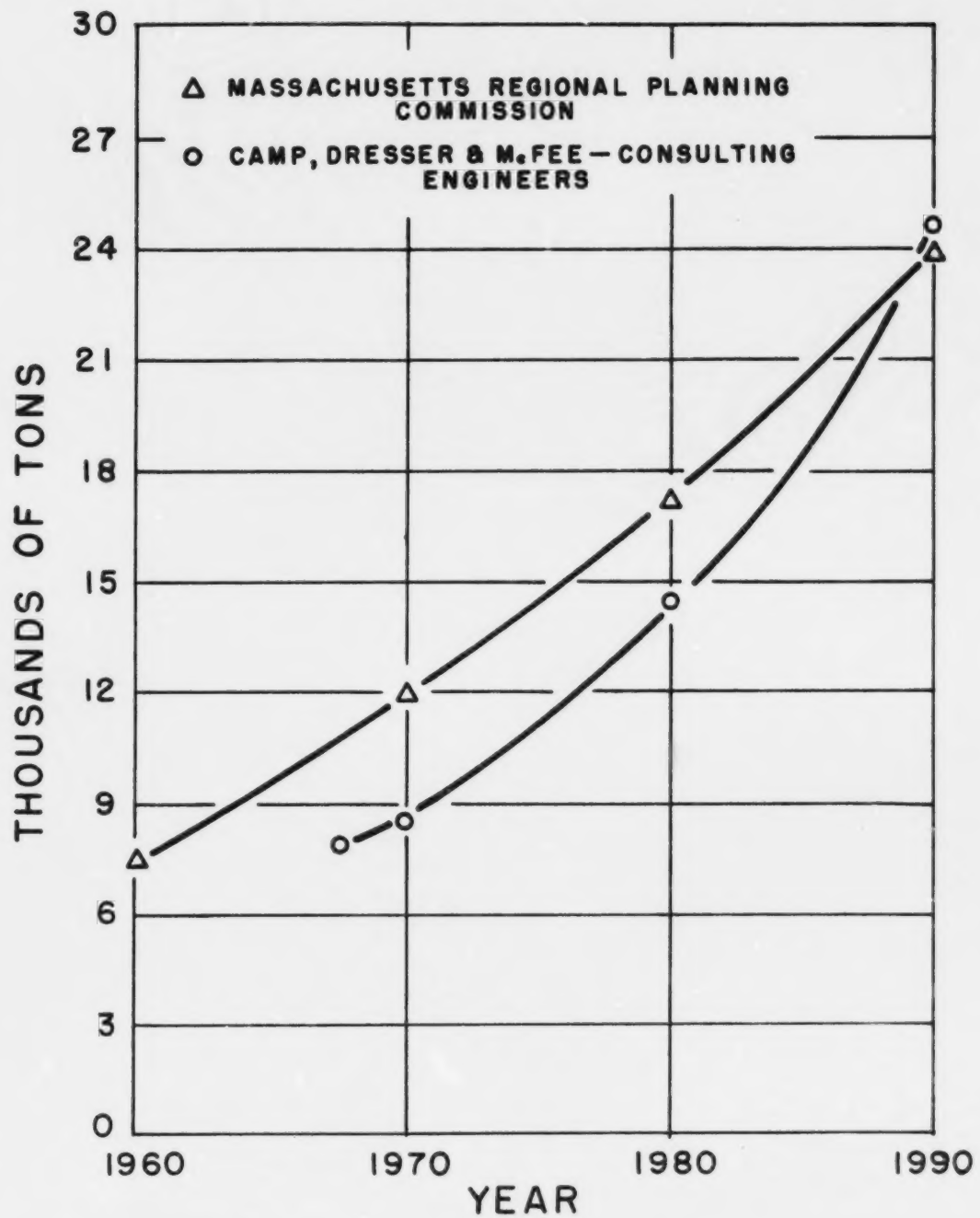


Figure 55

A study was authorized in 1969 by the town to determine the relative daily usage of the Sanitary Landfill. Table 30 summarizes these results.

Table 30
WEEKLY REFUSE DISTRIBUTION^a

	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
Tons	12	9.0	12	7.0	10	30	20.0
Cubic yards	8.5	7.0	12.5	7.0	10	32	23
Vehicles	7.0	3.5	8	3.5	11	32	35

^aAll numbers represent % of total

As would be expected with a private collection system, most of the refuse is brought to the landfill during the weekend.

CELLULOSE LIQUEFACTION AND HOLDEN

The Sanitary landfill presently used by the Town of Holden has an estimated life of 12-14 years. Since the town is situated in a water supply watershed which is used for Holden, Worcester and the Metropolitan District (Boston and others) the selection of a new landfill site within the town would be extremely difficult. Therefore, the town should be looking ahead to other methods of refuse disposal in order to solve its future disposal problems.

The design study considers the building of a solid waste liquefaction plant within the Town of Holden as a means of controlling its present and future refuse disposal problems. The advantages to the town are many, two major ones are listed below:

(1) Increased landfill life

The solid waste liquefaction plant will use all of the combustibles (and garbage) that constitute municipal refuse as a feedstock.

If such a plant is in operation, only inorganics (metal, glass, etc.) and a small amount of char (produced by the plant) need be landfilled. Recycling operations could even eliminate the need to landfill much of the metal and glass.

(2) Oil Utilization

The oil produced by the process could be used by the town to heat its schools, town halls, and other public buildings.

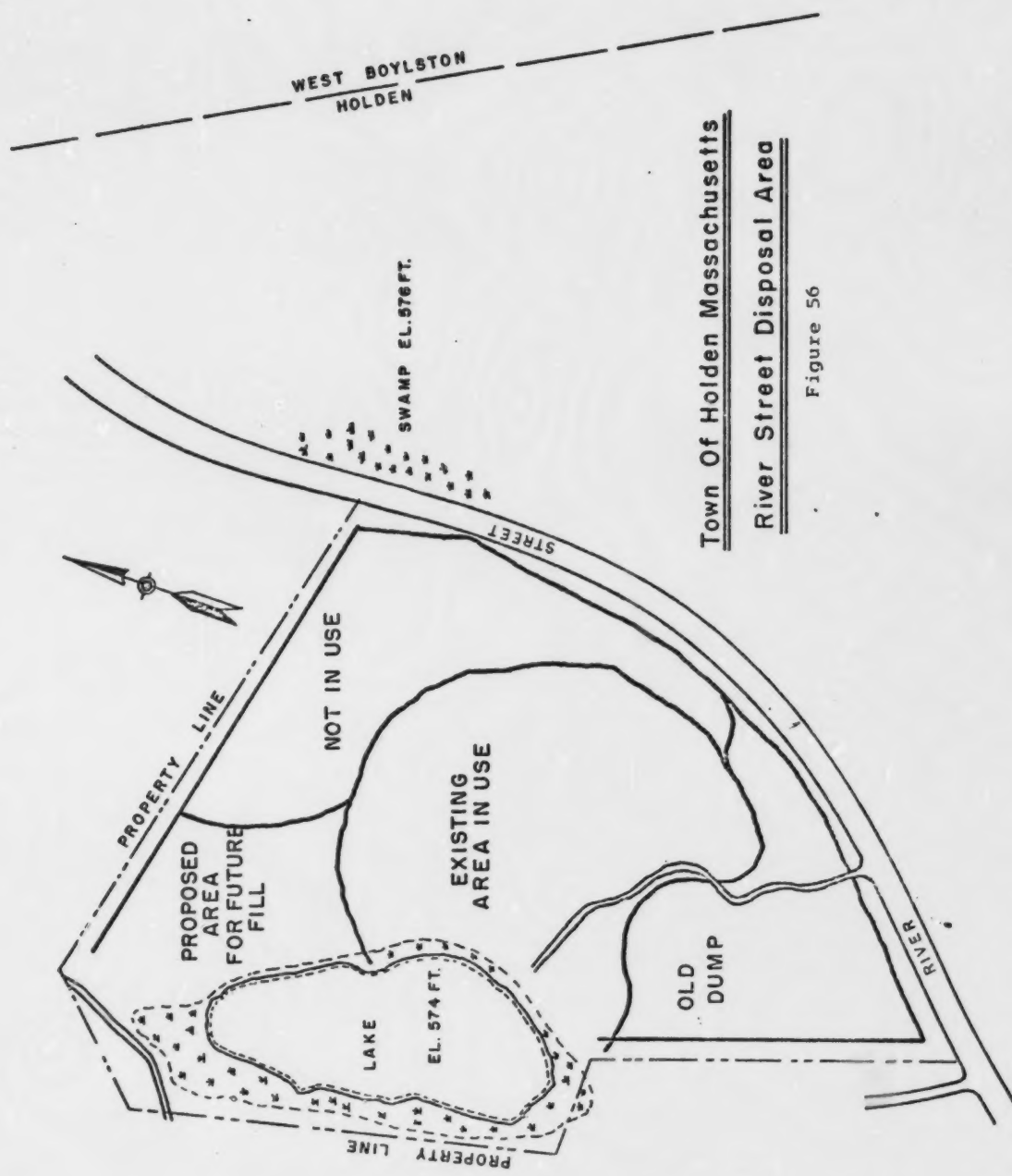
DESIGN CONSIDERATIONS

Plant Size

In the sizing of the plant care must be taken to allow room for future expansion as the amount of solid waste generated by the town of Holden increases. Therefore, the plant has been designed to handle 36 tons of combustibles (including garbage) per day. If the plant is operated 5 days/week it will be able to completely take care of the solid waste presently generated by the town and expansion can be accomplished by increasing operations to 7 days/week. If operations are expanded to 7 days/week, the plant will be of adequate size until the year 1980.

PLANT LOCATION

The plant could be located in the area marked "not in use" on Figure 56, the map of the River Street Sanitary Landfill site. This location of the plant is very advantageous because of the proximity to the landfill. Any inorganics which are not accepted as feed, as well as any char produced by the plant can easily be landfilled. Also in the event of a major breakdown in the plant, all refuse could be sent directly to the landfill.



Town Of Holden Massachusetts
River Street Disposal Area

Figure 56

FEED PREPARATION

The feed to the reactor is composed of combustible refuse slurried in oil. Therefore, the "raw" refuse which is brought to the plant must undergo preparation operations before it can be used.

Figure 57 is a diagram of the type of feed preparation system applicable to the Holden Plant. This system is consistent with the private refuse disposal system employed by the town of Holden. Individuals may drive up and deposit refuse on a conveyor where it will be taken for further processing. One problem is inorganics. If metals and other inorganics (glass, etc.) were accepted in the feed, an expensive separating system would have to be installed. Therefore, in an effort to keep costs at a minimum, only combustibles (paper, garbage, vegetation, etc.) will be accepted as feed to the plant. This requires residents to separate non-combustibles from combustibles, as is the practice in the neighboring city of Worcester, Mass.

The combustible refuse is ground in a hammer mill and stored in a silo until it can be slurried in oil (at a constant feed rate - to ensure continuous operation of the plant). This slurry constitutes the feed to the chemical processing section of the plant.

Since 50% of the weekly refuse total arrives at the plant during the weekend (Table 30), there must be storage capacity. This is provided by the pre-grinder storage area (which also allows room for private contractors to dump the refuse they have collected) and the storage silo. No health problems are expected by the storage of pulverized refuse for short amounts of time because pulverizing destroys flies, eggs and larvae. Rats do not live or breed in pulverized refuse. Pulverized material has a faint,

FEED PREPARATION SYSTEM

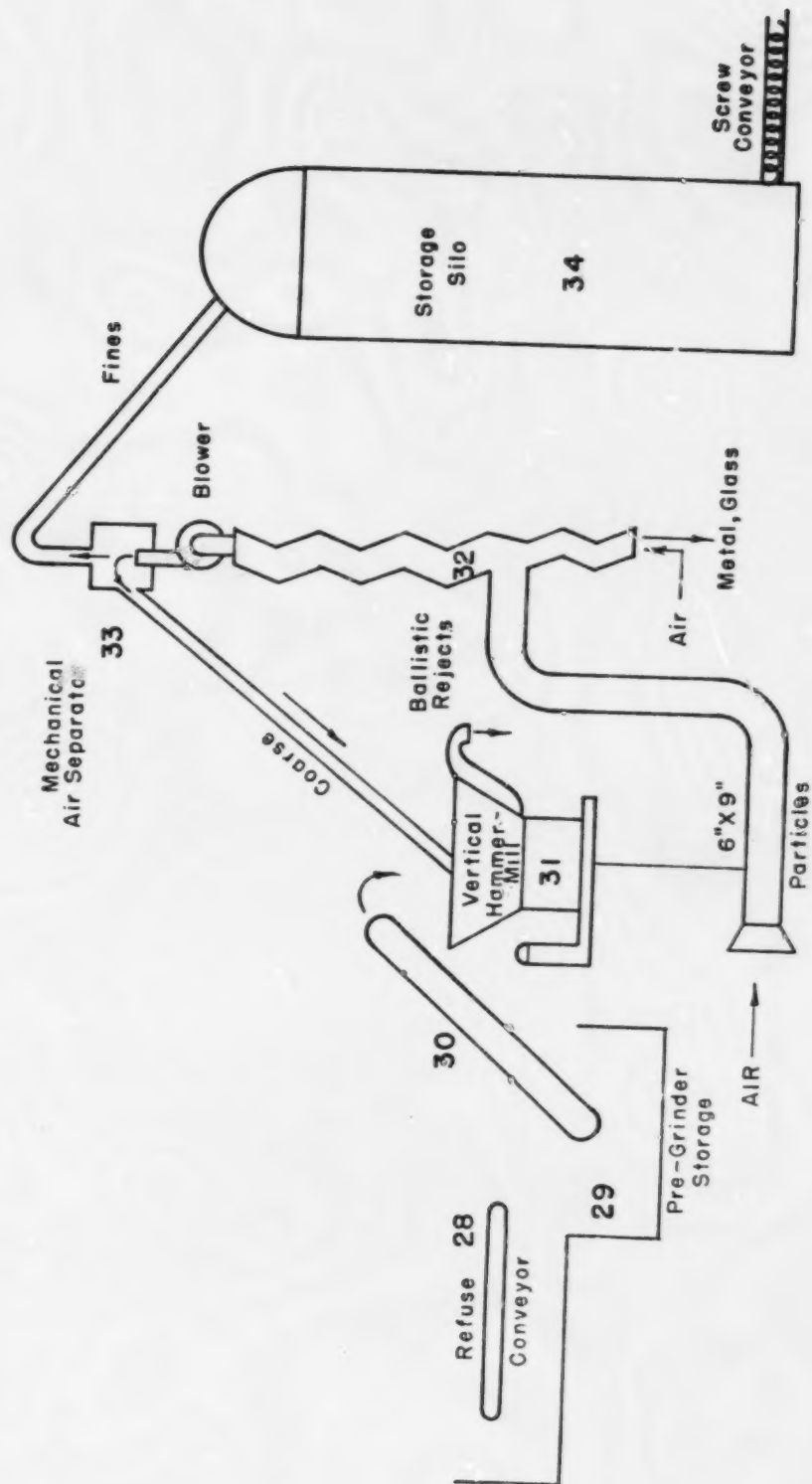


Figure 57

pleasant odor of freshly turned soil. The conveyor design should allow room for the peak number of vehicles to be able to deposit their refuse with a minimum of waiting and congestion.

PROCESSING SECTION

Using the pilot plant data previously presented in Table 28 of this report, the processing conditions for the plant were chosen. It is seen that the reactor conditions 452°C, 70 atm. H_2 , and 15.1 min space time give the best yield of oil, equivalent to 2.15 Bbl oil per ton refuse (moisture and combustibles only). These are the conditions which will be used in the operation of the 36 tons per day plant.

Nickel hydroxide, found to be a highly effective catalyst in laboratory and catalyst screening work, will be used as the catalyst in this plant.

The percentage of solids in the feed slurry is also an important design parameter. However, due to the small size of the pilot plant and problems such as clogging of lines, etc., only slurries of 20 wt. percent solids in oil can be used. It is estimated that the 36 ton per day plant could operate on slurries in the 25 to 50 wt. percent range. Therefore, the plant has been designed to process a 50% (by weight) refuse in oil slurry.

FLOW SHEETS AND MATERIAL BALANCES

The process consists of five main operations: feed preparation, liquefaction reaction, hydrogen preparation, product recovery, and water purification-nickel recovery. Figure 58 is a process flow diagram showing the interconnection of the equipment involved in the process. The areas outlined by dotted lines correspond to the major operations described above. Figures 57 and 59 show the feed preparation and water purification-nickel recovery sections (not included in the main drawing) respectively.

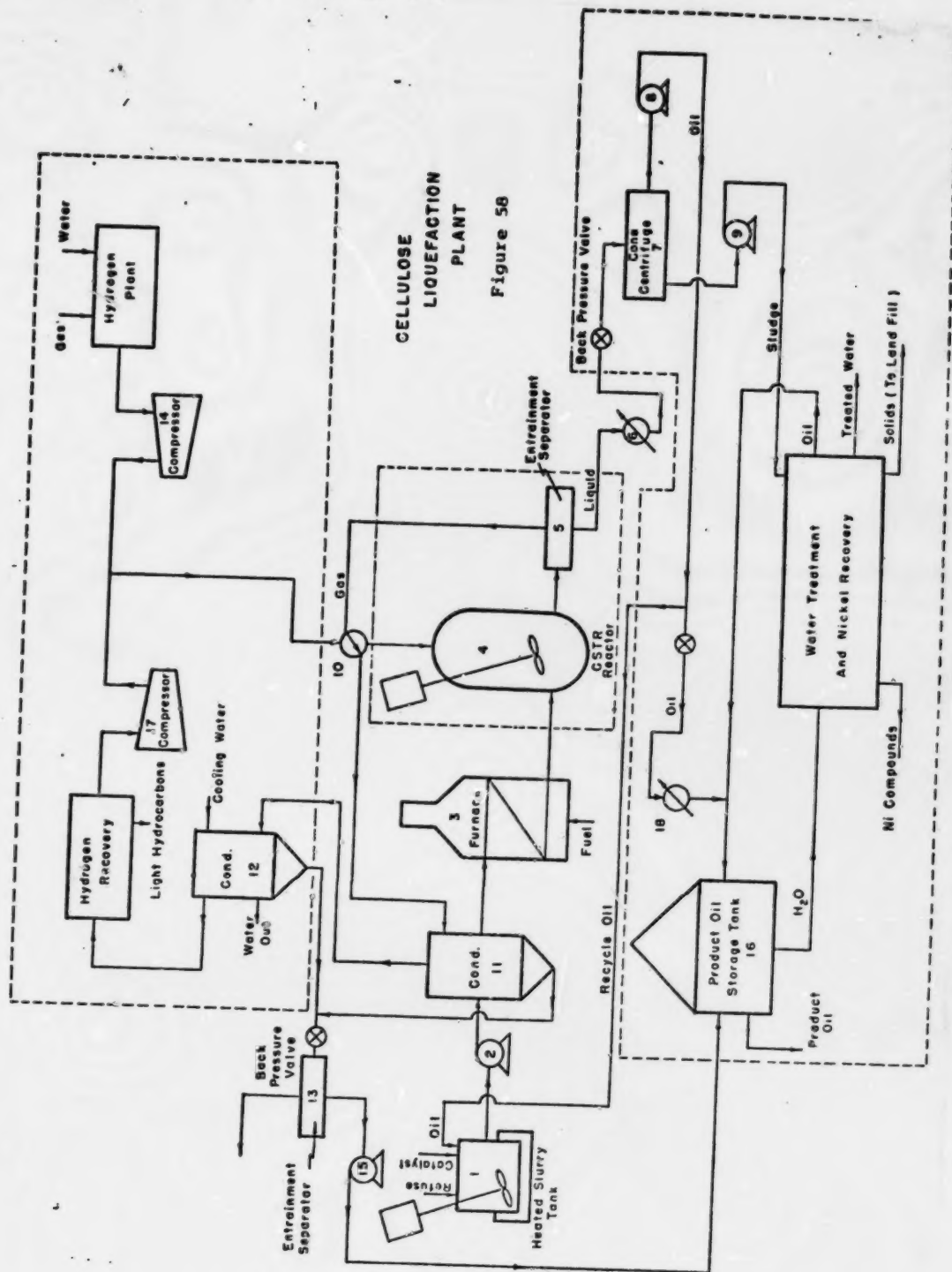
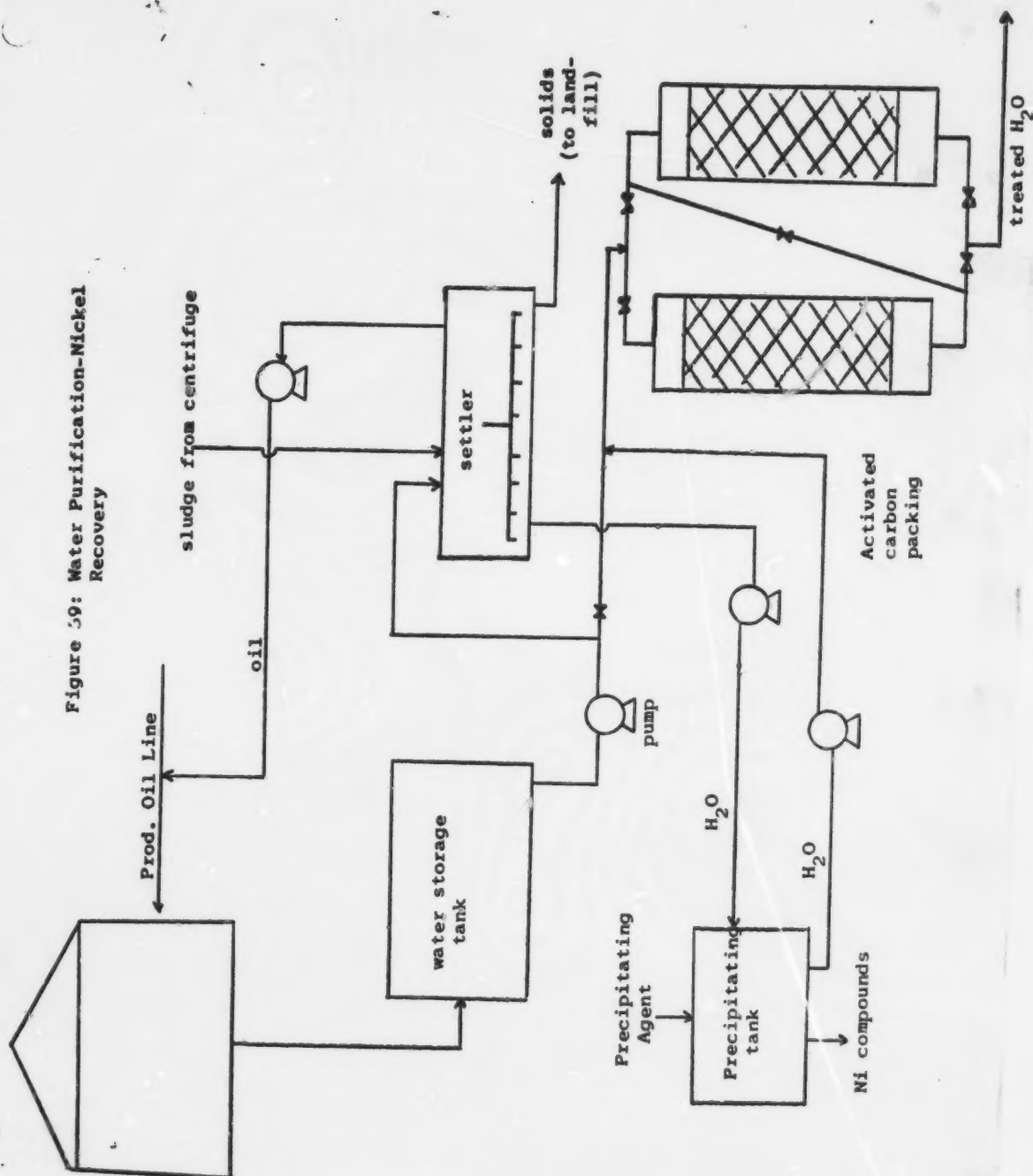


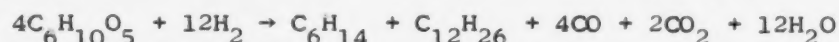
Figure 59: Water Purification-Nickel Recovery



Briefly each section is expected to accomplish the following:

a) Feed Preparation - refuse is ground in a hammer mill and stored in a silo until it can be slurried in oil (at a constant feed rate). The mechanical air separator is included to ensure uniform feed particle size.

b) Liquefaction Reaction - Using pilot plant data, an overall material balance for the 36 ton per day plant is presented in Figure 60. A rough approximation of the complex stoichiometry of the reaction is:



The purpose of the above equation is informative. The glucose formula is used to model solid waste, and the six- and twelve-carbon hydrocarbon products represent low and high boiling product components (but, by no means, pure hexane and dodecane!!). The importance of the stoichiometry is that it shows CO and CO₂ formation proceeding in-situ, implying the water gas shift reaction:



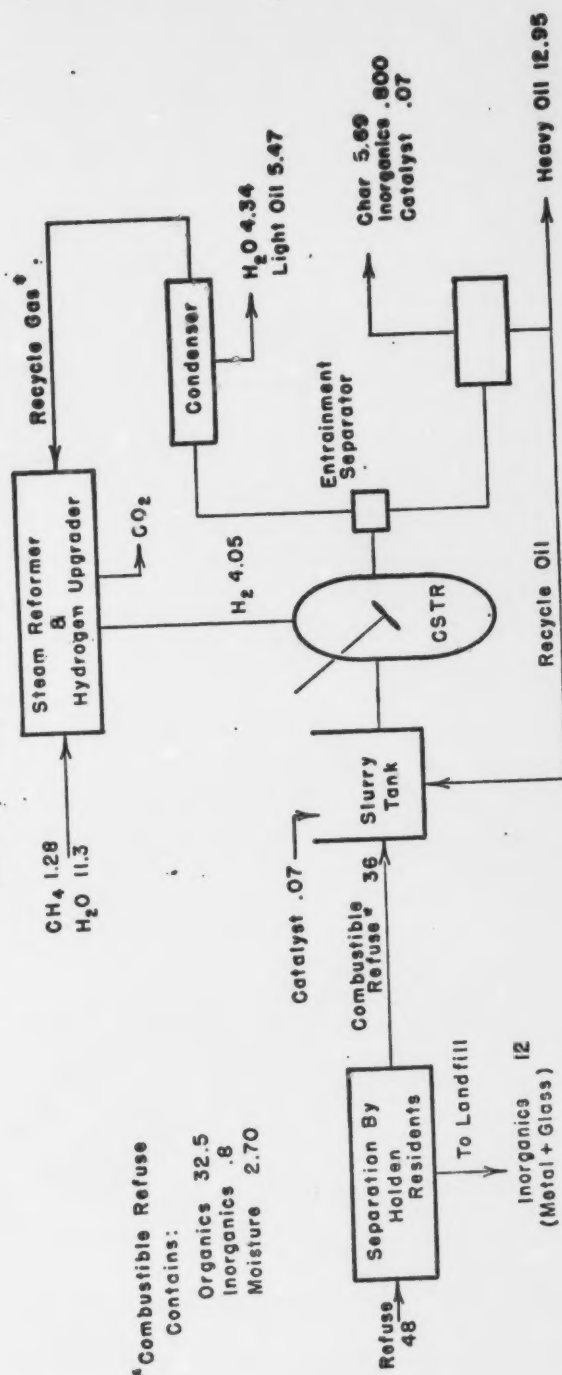
takes place.

c) Hydrogen Preparation - The reactor is a net consumer of hydrogen, so makeup hydrogen must be continuously fed to the reactor. This is accomplished by the Hydrogen Plant and an ethanolamine scrubber. The scrubber removes CO₂ and light hydrocarbons (by refrigeration) thus allowing the recycling of unused hydrogen. The hydrogen plant produces hydrogen by steam reforming in amounts needed to maintain the partial pressure of hydrogen in the reactor. The light hydrocarbons produced in the reactor can be used as a feed to this plant.

d) Product Recovery - The product recovery system separates liquids, solids, and gases and is comprised of only well known chemical engineering unit operations such as solids separation (by centrifuge), heat transfer, etc.

OVERALL MATERIAL BALANCE

All Numbers in Tons/Day



* Combustible Refuse
Contains:
Organics 32.5
Inorganics .8
Moisture 2.70

* Recycle Gas Contains:

CO 3.34
CO₂ 2.40
CH₄ .036
C₂-C₄ 2.56
H₂ 2.34

Figure 60

e) Water Purification-Nickel Recovery - The water produced in the process must be treated before being discharged since it may be contaminated with organic compounds produced in the process. Investigation has shown that absorption into activated carbon is an effective method for this type of water treatment. Experiments to date show that inorganics put into the process (catalysts and others from the refuse) come out of the process with the water as a sludge. The sludge is steamed and landfilled. Since it is sterile, it does not contribute to ground water pollution. Although not shown on the flowsheets, two sub-systems are also included within the plant. The first is the activated carbon regeneration system. Carbon is regenerated by passing heated air through the adsorber column. This heated air is used as an input to the process furnace, thus burning the entrained organics to harmless CO_2 and H_2O . The second sub-system is the cooling water system. (Since the location of the plant makes necessary the use of an external system utilizing a spray, a pond is included in the design.) Water lost from the spray pond will be replenished by water produced in the reactor, making the total cooling water requirements approximately zero.

The process is considered to be virtually pollution free. The only effluents from the plant are clean water, CO_2 , and deactivated sludge.

Plant Layout

Figure 61 represents an estimate of the overall outside dimensions of the plant and equipment placement. For safety reasons, the public will not be allowed within the boundaries of the plant during operation. The conveyor on which refuse is deposited will be located outside the confines of the plant. Examination of the figure shows that the grinder is located

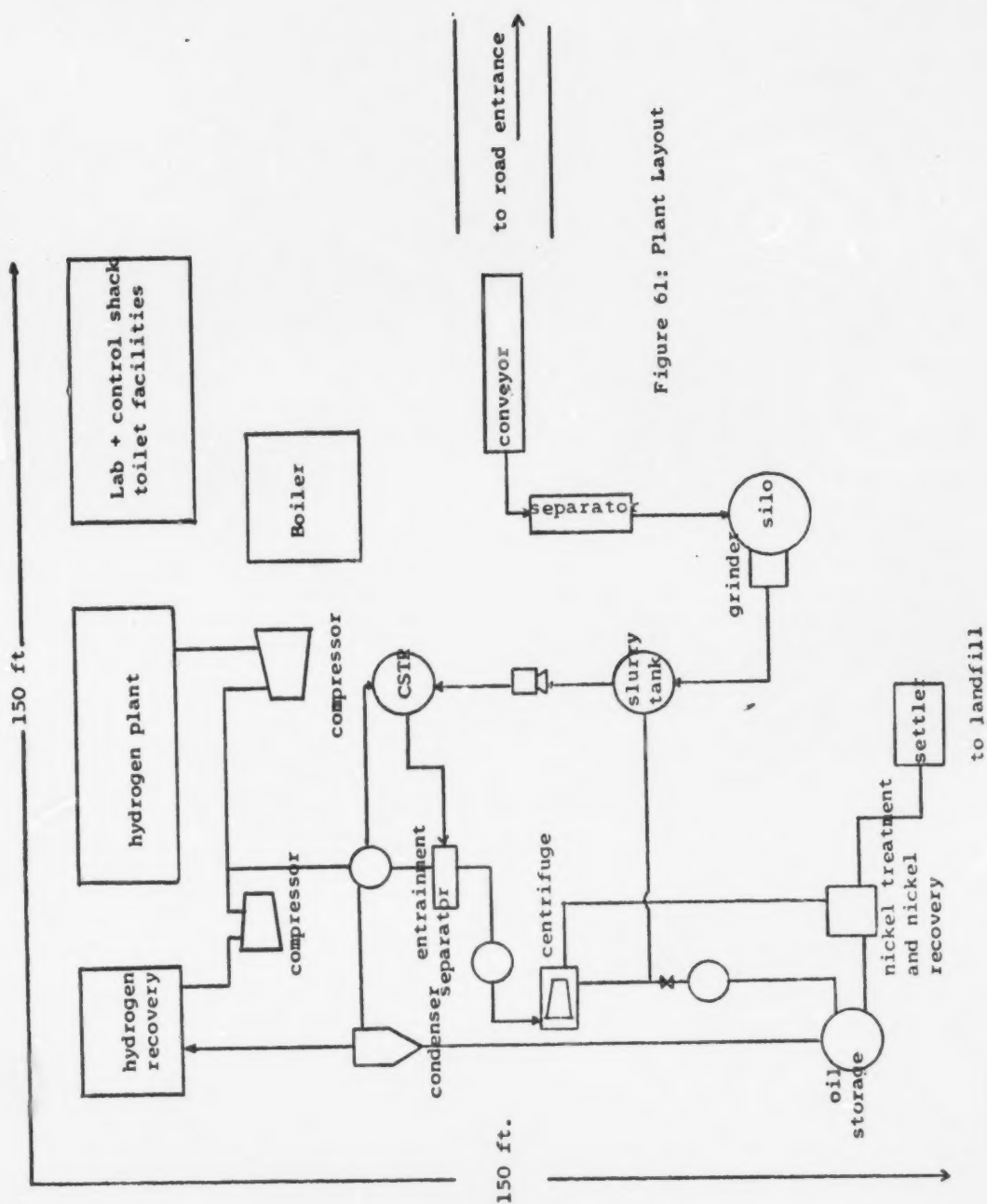


Figure 61: Plant Layout

away from the population center of the plant (control and laboratory facilities). This is also necessary for health reasons.

EQUIPMENT

The most important part of this design is the equipment selection and specification. For the purposes of safety and flexibility, many of the pieces of equipment were overdesigned, i.e., conditions more severe than those actually expected are specified on the sheets which follow.

Tank

Identification: Heated Slurry Tank
Item No. 1
No. Required 1
Function: To prepare the feed slurry
Operation: Continuous
Type: Jacketed and Agitated Vessel
Carbon Steel
Size: 750 gallons with 40 HP motor for Agitator
Utilities: Electricity
Purchased equipment cost (ft note 1): \$6,400

Pump

Identification: Pump
Item No. 2
No. Required 1
Function: To pump the feed slurry to 1,000 PSIA
Operation: Continuous
Type: Moyno
Details: GPM 12.3
Liquid 60.5 lb/ft³
Discharge pressure 1,000 PSIA
Heat 985.36 PSIA 2,100 ft of liquid
HP 30
Utilities: Electricity
Purchased equipment cost (ft note 2): \$6,900

Furnace

Identification: Furnace
Item No. 3
No. Items Required 1
Function: To heat feed slurry
Operation: Continuous
Type: Cylindrical Direct Fired Heaters
Duty 2,560,000 Btu/hr
Tube Side: Fluid Handled - feed slurry
Flow rate 12.3 gpm
Pressure 1,500 PSIG
Temperature 440°F → 800°F
Tube Material Stainless Steel
Utilities: Natural Gas fuel or Product Oil Fuel
Purchased equipment cost (ft note 3) \$23,800

Reactor

Identification: CSTR Reactor
Item No. 4
No. required 1
Operation: Continuous
Type: Continuous stirred tank reactor (CSTR)
Size: 3 ft. diameter x 5 ft. height (Basis 4 LHSV)
Details: Stainless steel 316
Allowable stress 16 (ASME code, Section VIII, Div. II)
Pressure 1,500 psig
Wall thickness 2.25"
10 HP agitator
Weight: Weight of vessel 6000 lb
Weight of heads 6000 lb
Utilities: Electricity
Purchased equipment cost (ft. note 4): \$14,400

Entrainment Separator

Identification: Entrainment Separator
Item No. 5
No. required 1
Function: To separate the gas and liquid products
Operation: Continuous
Type: Horizontal line installed
No. LCS - 150- 1500 (V.D. Anderson Co., Cleveland, Ohio)
5 $\frac{1}{2}$ " diameter x 17" length
1 $\frac{1}{2}$ " weld
304 L stainless steel
Details: 70,000 ScfH gas (Ave. mol. wt. x 15 lb/lb mol)
3680 lb/hr liquid
Design pressure 1,500
Design temperature 1000°F
Purchased equipment cost (ft. note 5): \$5,400

Heat Exchanger

Identification: Heat Exchanger
Item No. 6
No. required 1
Function: To cool the product liquid from reaction temperatures
Operation: Continuous
Type: Horizontal
Straight tube
Fixed tube sheet
Duty 1,750,000 Btu/hr Transfer area 103.7 ft²
Tube Side: Fluid Handled - product oil
Flow Rate - 3,500 lb/hr
Pressure - 2,500 PSI
Temperature - 850°F - 200°F
Tube Material - Stainless steel 316
2 passes
Shell Side: Fluid Handled - Cooling water
Flow rate - 31 gpm
Pressure - 300 PSIG
Temperature - 80°F - 190°F
Shell material - Carbon steel
Utilities: Untreated cooling water
Purchased equipment cost (ft. note 6): \$9,050

Centrifuge

Identification: Continuous Centrifuge
Item No. 7
No. required 1
Function: To remove solids from the liquid product
Operation: Continuous
Type: Solid Bowl Stainless steel
Details: HP 5
Liquid 3,500 lb/hr
Solids 150 lb/hr
Utilities: Electricity
Purchased equipment cost (ft. note 7): \$11,400

Pump

Identification: Pump
Item No. 8
No. required 1
Function: To pump products into the storage tank
Operation: Continuous
Type: Centrifugal
Details: gpm 10
ρ liquid 50 lb/ft³
Discharge pressure 29 PSIA
Head 13.96 PSIA 23.8 ft. of liquid
HP 1/4
Utilities: Electricity
Purchased equipment cost (ft. note 8): \$750

Pump

Identification: Pump
Item No. 9
No. required 1
Function: To pump sludge to settling tank
Operation: Continuous
Type: Centrifugal
Details: gpm 1/2
 ρ liquid 80 lb/ft³
Discharge pressure 29 PSIA
Head 13.96 PSIA 37.8 ft. of liquid
HP 1/4
Utilities: Electricity
Purchased equipment cost (ft. note 8): \$750

Heat Exchanger

Identification: Heat Exchanger
Item No. 10
No. required 1
Function: To cool product gas and heat feed hydrogen
Operation: Continuous
Type: Verticle
Straight tube
Floating tubesheet bundle
Duty 715,000 Btu/hr Transfer area 52 ft²
Tube Side: Fluid handled Product gas
Flow rate 2510 lb/hr
Pressure 3000 PSI
Temperature 865°F → 850°F
Tube material Stainless steel 316
2 passes
Shell Side: Fluid handled Feed hydrogen
Flow rate 410 lb/hr
Pressure 3000 PSI
Temperature 103°F → 690°F
Shell material Stainless steel 316
Purchased equipment cost (ft. note 6): \$14,300

Heat Exchanger

Identification: Condenser
Item No. 11
No. required 1
Function: To cool product gas and heat feed hydrogen
Operation: Continuous
Type: Verticle
Straight tube
Floating tubesheet bundle
Duty 715,000 Btu/hr Transfer area 52 ft²
Tube Side: Fluid handled Product gas
Flow rate 2510 lb/hr
Pressure 3000 PSI
Temperature 865°F → 850°F
Tube material Stainless steel 316
2 passes
Shell Side: Fluid handled Feed hydrogen
Flow rate 410 lb/hr
Pressure 3000 PSI
Temperature 103°F → 690°F
Shell material Stainless steel 316
Purchased equipment cost (ft. note 6): \$14,300

Heat Exchanger

Identification: Condenser
Item No. 11
No. required 1
Function: To condense light oil and water from product gas and heat
feed slurry
Operation: Continuous
Type: Horizontal
Straight tube
Fixed tube sheet
Duty 14,300 Btu/hr Transfer area 2010 ft²
Tube Side: Fluid handled Feed slurry
Flow rate 12.3 gpm
Pressure 2000 PSI
Temperature 200°F → 440°F
Tube material Stainless steel 304
Shell Side: Fluid handled Product Gas
Flow rate 2510 PSI
Pressure 2000 PSI
Temperature 850°F → 230°F
Shell material Carbon Steel
Purchased equipment cost (ft. note 9): \$23,000

Heat Exchanger

Identification: Condenser
Item No. 12
No. required 1
Function: To condense light oil and water from product gas
Operation: Continuous
Type: Horizontal
Straight tube
Fixed tube sheet
Duty 119,000 Btu/hr Transfer area 94.5 ft²
Tube Side: Fluid handled Cooling water
Flow rate 6 gpm
Pressure 300 PSI
Temperature 80°F → 120°F
Tube material Carbon steel
2 passes
Shell Side: Fluid handled Product gas
Flow rate 1200 lb/hr
Pressure 2000 PSI
Temperature 229°F → 82°F
Shell material Carbon steel
Utilities: Untreated cooling water
Purchased equipment cost (ft. note 9): \$1,150

Entrainment Separator

Identification: Entrainment Separator
Item No. 13
No. required 1
Function: To separate the gas from liquid out of the condenser
Operation: Continuous
Type: Horizontal line installed
No. LC-200 (V.D. Anderson Co., Cleveland, Ohio)
Details: 4,000 ScFh gas (ave. mol. wt. 15/lb/lb mol)
265 lb/hr liquid
Design pressure 14.7 PSIA
Design temperature 80°F
Purchased equipment cost (ft. note 5): \$300

Compressor

Identification: Compressor
Item No. 14
No. required 1
Function: To compress make-up hydrogen to 1000 PSIA
Operation: Continuous
Type: Reciprocating
Details: Input pressure 350 PSI
Max. output pressure 5000 PSI
Cast iron construction
HP 45
Utilities: Electricity
Untreated cooling water
Purchased equipment cost (ft. note 10): \$16,350

Pump

Identification: Pump
Item No. 15
No. required 1
Function: To pump products into the storage tank
Operation: Continuous
Type: Centrifugal
Details: gpm 3.2
 ρ liquid 50 lb/ft³
Discharge pressure 29 PSIA
Head 13.96 PSIA 23.8 ft. of liquid
Utilities: Electricity
Purchased equipment cost (ft. note 8): \$750

Tank

Identification: Storage Tank
Item No. 16
No. required 1
Function: To store the product oil
Type: Horizontal tank
Carbon steel
Size: 20,000 gal.
Purchased equipment cost (ft. note 11): \$4,100

Compressor

Identification: Compressor
Item No. 17
No. required 1
Function: Compress purified hydrogen to 1,000 PSIA
Operation: Continuous
Type: Reciprocating
Details: Input pressure 600 PSIG
Max. output pressure 5,000 PSI
Cast iron construction
HP 25
Utilities: Electricity
Purchased equipment cost (ft. note 10): \$12,800

Heat Exchanger

Identification: Heat Exchanger
Item No. 18
No. required 1
Function: To cool the product oil before it reaches the storage tank
Operation: Continuous
Type: Horizontal
Straight tube
Fixed tube sheet
Duty 39,700 Btu/hr Transfer area 21.1 ft²
Tube Side: Fluid handled Product oil
Flow rate 750 lb/hr
Pressure 150 PSI
Temperature 152°F → 94°F
Tube material Carbon steel
2 passes
Shell Side: Fluid handled Cooling water
Flow rate 1.2 gpm
Pressure 150 PSI
Temperature 80°F → 120°F
Shell material Carbon steel
Utilities: Untreated cooling water
Purchased equipment cost (ft. note 6): \$700

Water Storage Tank

Identification: Water Storage Tank
Item No. 19
No. required 1
Function: To store water coming from oil storage tank
Type: Horizontal tank
Carbon steel
Size: 5,000 gals.
Purchased equipment cost (ft. note 11): \$2,800

Boiler

Identification: Boiler
Item No. 20
No. required 1
Function: To provide steam for use throughout the plant
Operation: Continuous
Size: 1,000 lb steam/hr
Details: Fuel burning
Forced draft
Utilities: Natural gas fuel or product oil fuel
Purchased equipment cost (ft. note 13): \$4,100

Tower

Identification: Adsorption Tower
Item No. 21
No. required 2
Function: Treatment of water
Operation: Continuous
Type: Steel
Size: 70 cu. ft., 3 ft. diameter x 9 ft. height
Purchased equipment cost (ft. note 12): \$5,300

Tank

Identification: Settling Tank
Item No. 22
No. required 1
Function: To settle out solids and recover catalyst salts
Operation: Batch (automatic)
Type: Agitated tank
Size: 350 gal. with 10 HP motor for agitator
Utilities: Electricity
Purchased equipment cost (ft. note 12): \$7,900

Tank

Identification: Precipitation tank
Item No. 23
No. required 1
Function: To act as a reactor for precipitation of catalyst salts
Operation: Batch (automatic)
Type: Agitated vessel
Carbon steel
Size: 350 gal. with 1 HP motor for agitator
Utilities: Electricity
Purchased equipment cost (ft. note 12): \$7,900

Pump

Identification: Pump
Item No. 24
No. required 3
Function: To cycle the water in the purification system
Operation: Continuous
Type: Centrifugal
Details: gpm 19.5
p liquid 63 lb/ft²
Discharge pressure 29 PSIA
HP 1/4
Utilities: Electricity
Purchased equipment cost (ft. note 14): \$4,800

Gas Storage Tank

Identification: Tank
Item No. 25
No. required 1
Function: Storage of gas for use throughout the plant
Type: Horizontal pressure storage vessel
Carbon steel
Design pressure 150 PSI
Size: 5,000 gal.
Purchased equipment cost (ft. note 14): \$4,800

Spray Pond

Identification: Spray Pond
Item No. 26
No. required 1
Function: Cool water to be used as cooling water throughout plant
Operation: Continuous
Type: Buried tank 12' x 5' x 3'
3 Spray nozzles (5 PSIA pressure)
Enclosed by 6 ft. louver fence
Perpendicular to prevailing winds
Details: Water is cooled 40°F
Purchased equipment cost (ft. note 15): \$2,500

Pump

Identification: Cooling System Pump
Item No. 27
No. required 1
Function: To pump cooling water to plant
Operation: Continuous
Type: Centrifugal
Details: gpm 50
 ρ liquid 62.4 lb/ft³
Discharge pressure 50 PSIA
HP 3/4
Utilities: Electricity
Purchased equipment cost (ft. note 8): \$1000

Conveyor

Identification: Refuse conveyor
Item No. 28
No. required 1
Function: To convey refuse from private cars to the pre-grinding storage
Operation: Continuous (8 hrs/day)
Type: Belt conveyor
Size: 30 ft. long x 30" belt
Utilities: Electricity
Purchased equipment cost (ft. note 16): \$4,200

Gas Storage Tank

Identification: Tank
Item No. 25
No. required 1
Function: Storage of gas for use throughout the plant
Type: Horizontal pressure storage vessel
Carbon steel
Design pressure 150 PSI
Size: 5,000 gal.
Purchased equipment cost (ft. note 14): \$4,800

Spray Pond

Identification: Spray Pond
Item No. 26
No. required 1
Function: Cool water to be used as cooling water throughout plant
Operation: Continuous
Type: Buried tank 12' x 5' x 3'
3 Spray nozzles (5 PSIA pressure)
Enclosed by 6 ft. louver fence
Perpendicular to prevailing winds
Details: Water is cooled 40°F
Purchased equipment cost (ft. note 15): \$2,500

Pump

Identification: Cooling System Pump
Item No. 27
No. required 1
Function: To pump cooling water to plant
Operation: Continuous
Type: Centrifugal
Details: gpm 50
ρ liquid 62.4 lb/ft³
Discharge pressure 50 PSIA
HP 3/4
Utilities: Electricity
Purchased equipment cost (ft. note 8): \$1000

Conveyor

Identification: Refuse conveyor
Item No. 28
No. required 1
Function: To convey refuse from private cars to the pre-grinding storage
Operation: Continuous (8 hrs/day)
Type: Belt conveyor
Size: 30 ft. long x 30" belt
Utilities: Electricity
Purchased equipment cost (ft. note 16): \$4,200

Storage

Identification: Pre-grinder storage
Item No. 29
No. required 1
Function: To store refuse before it enters the hammermill
Operation: Continuous
Size: 90 cubic yards
Purchased equipment cost (ft. note 11) \$5400

Hammermill

Identification: Hammermill and feed conveyor
Items No. 30 and 31
No. required 1
Function: To grind refuse
Operation: Continuous (8 hrs/day)
Size: 4.5 tons/hr
90 HP motor
Utilities: Electricity
Purchased equipment cost (ft. note 11) \$80,000

Elevator

Identification: Classifier
Item No. 32
No. required 1
Function: To remove metal and glass from ground solid waste
Operation: Continuous
Type: Zig zag
Utilities: Electricity
Purchased equipment cost (ft. note 16): \$500

Separator

Identification: Mechanical air separator
Item No. 33
No. required 1
Function: To separate the pulverized refuse by particle size
and recycle oversized particles to grinder
Operation: Continuous
Size: 6 tons/hr
10 ft. inside diameter x 16 ft. height
25 HP motor
Utilities: Electricity
Purchased equipment costs (ft. note 7): \$15,000

Storage

Identification: Storage Silo
Item No. 34
No. required 1
Function: To store pulverized refuse (feed) until it can be used
in process
Size: 285 cubic yards
Purchased equipment cost (ft. note 11) \$13,000

Conveyor

Identification: Screw Conveyor
Item No. 35
No. required 1
Function: To feed refuse into slurry tank at constant rate
Operation: Continuous (24 hrs/day)
Size: 10 ft. long - 9" screw
Utilities: Electricity
Purchased equipment costs (ft. note 17): \$1,000

Compressor

Identification: Compressor
Item No. 36
No. required 1
Function: To pump heated air through the activated carbon
absorption towers
Operation: Continuous
Type: Centrifugal
Details: Max. output pressure 125 psig
10 cu. ft./min. of air
HP 10
Utilities: Electricity
Purchased equipment cost (ft. note 13): \$5,500

Steam Reforming Hydrogen Plant

Function: To produce hydrogen by steam reforming
Operation: Continuous
Type: Steam reforming hydrogen
(C&I/Girdler Inc.)
Details: 131 lb/hr = 575,000 scfd
Operating pressure 350 PSIG
Hydrogen product purities 90-95%
Packaged Cost: \$98,500

Hydrogen Recovery System

Function: To recover hydrogen from condenser off-gas
Operation: Continuous
Type: Low purity hydrogen upgrader
(Linde Div. of Union Carbide)
Details: 191 lb/hr = 820,000 scfd
Operating pressure 600 PSIG
Hydrogen product purities 90-98%
Hydrogen recovery efficiency 99%
Packaged Cost: \$67,500

Cost Footnotes

1. Popper, H., "Modern Cost-Engineering Techniques," McGraw Hill Book Co. N.Y., p. 189, 1970.
2. Ibid, p. 149
3. Ibid, p. 87
4. Clark, F.D., and Terni, S.P., Thick Wall Pressure Vessels, Chemical Engineering, Vol. 79, No. 6, p. 112, 1972.
5. Quote from V.D. Anderson Co., Cleveland, Ohio.
6. Popper, H., "Modern Cost-Engineering Techniques," McGraw Hill Book Co., N.Y., p. 189, 1970.
7. Ibid, p. 98,99
8. Ibid, p. 115
9. Ibid, p. 450
10. Ibid, p. 150
11. Ibid, p. 117
12. Ibid, p. 190
13. Ibid, p. 132
14. Ibid, p. 107
15. Ibid, p. 100, 116
16. Ibid, p. 129
17. Ibid, p. 132
18. Quote from Francis and John S. Lane Limited, England.

Utilities Needed

Based upon the specified equipment and operating conditions, Table 31 represents a summary of the utilities needed for the operation of the plant.

Since water is cooled in the spray pond and the loss replenished by that made in the reaction, the total amount needed is zero. The water needs listed on the summary sheet represent the relative amounts used by each piece of equipment. These figures were used in designing the internal cooling water system.

Product oil could be used instead of natural gas. Therefore the amount of oil which would be equivalent to natural gas is also listed in Table 31.

Table 31. UTILITIES SUMMARY - 50% SLURRY

Equipment	Description	Water	Natural Gas	Electricity
1. Heated Slurry Tank	40 HP motor			716 KWH/day
2. Pump	30 HP motor			540
3. Furnace	uses natural gas as fuel		2.93x10 ³ a ft ³ /hr	
4. CSTR Agitator	10 HP motor	1850 gal/hr**		179
6. Heat Exchanger	5 HP motor			89
7. Continuous Centrifuge	1/4 HP motor			4.4
8. Pump	1/4 HP motor			4.4
9. Pump				
12. Condenser				
14. Compressor	45 HP motor	350 gal/hr**		805
15. Pump	1/4 HP motor	70 gal/hr**		4.4
17. Compressor	25 HP motor	70 gal/hr**		447.5
18. Heat Exchanger		70 gal/hr**		
20. Boiler	uses natural gas as fuel	135 gal/hr	1.0x10 ³ b ft ³ /hr	
22. Settling Tank	10 HP motor			179
23. Precipitation Tank	1 HP motor			17
24. Pumps (3)	1/4 HP motor			13
27. Pump	3/4 HP motor			13
28. Receiving and Grinding				
35. Compressor	115 HP motor			685 ~~7~~
36. Hydrogen Plant	10 HP motor			179
	uses natural gas as feedstock	139 gal/hr	6.3x10 ³ c ft ³ /hr	222
Hydrogen Recovery		238 gal/hr		190
			10.23x10 ³ ft ³ /hr	4287.7 KWH/day

* $\Delta T = 40^{\circ}\text{F}$ ** $\Delta T = 100^{\circ}\text{F}$ ~~7~~ operates on an 8 hour day

a) equivalent to .42 BBL oil/hr

b) equivalent to .14 BBL oil/hr

c) equivalent to .10 BBL/hr

OPERATION OF THE PILOT PLANT

Operation of the plant will be for 24 hours per day, five days per week, throughout the year. The remaining two days per week would be used for maintenance. Since Table 30 shows that the most refuse would be brought to the plant during the weekend, it must be required that the plant be operational during this time. Therefore, it is recommended that the operation of the plant be from Thursday through Monday, with Tuesday and Wednesday being the two shutdown days per week.

A deviation from the 24 hour/day schedule should be enforced for the particle size reduction system. Because the hammermill is noisy, the operation of this system is scheduled for only 8 hours/day (dayshift) to ease any discomfort which may be felt by the residents of the area. This requires that the entire day's refuse (36 tons) be processed in 8 hours and that the system must be capable of handling 4.5 tons refuse/hour. This has been taken into account in the design of the feed preparation system.

If, in order to increase capacity, operations were expanded to 7 days/week, a two week shutdown period every 6 months would be used for maintenance. All refuse would be landfilled during this period.

Personnel needed for the operation of the plant are outlined as follows:

	Total	Annual Salary*
Chief operator (1 per shift)	3	10,000
Asst. operator (1 per shift)	3	8,000
Plant engineer (on call at night)	1	15,000
Maintenance (" " " ")	1	10,000
Secretary	$\frac{1}{2}$	5,000
Equipment Operator (for landfill, receiving, & grinding)	1	8,000
Quality Control Chemist	$\frac{1}{2}$	12,000

*from "C.W. Report" by John M. Winton, Chemical Week, Oct. 11, 1972

If a shutdown occurs, the assistant operators will be used to aid the landfill operations.

The following are detailed job descriptions for the positions outlined above. They are based upon descriptions the town of Holden uses in its hiring of personnel.

Plant Engineer

Definition - Administrative and Supervisory work in connection with the operation of cellulose liquefaction plant.

Distinguishing Characteristics -

- works under the general supervision of the Town Manager
- exercises considerable judgement as to operation of plant
- makes frequent contact with Town Manager and quality control chemist in evaluating performance of plant
- errors could result in improper operation of plant, increasing costs of operation and/or maintenance.

Examples of Work -

- Supervise chief operators and oversee daily operation of plant
- Establish operational procedures for startup, shutdown, and regular operation

Desirable Qualifications -

- College graduate with a major in chemical engineering; five years experience as plant (production) engineer; or any equivalent combination of education and experience
- Ability to handle men

Quality Control Chemist

Definition - Performs analytical tests of cellulose liquefaction plant feedstock and products.

Distinguishing Characteristics

- works under general supervision of the plant engineer
- performs a variety of qualitative and quantitative chemical tests to determine compositions of products; exercises judgement in performing and evaluating analytical tests.
- makes frequent contact with plant engineer in evaluating overall performance of plant
- errors could jeopardize product quality

Examples of Work -

- determination of sulfur content of product oil
- determination of heating value of product oil

Desirable Qualifications -

- College graduate with a major in analytical chemistry; 5 years experience as an analytical chemist; or any equivalent combination of education and experience
- considerable knowledge of organic chemistry

Chief Operator

Definition - skilled technical work in connection with the operation of cellulose liquefaction plant

Distinguishing Characteristics -

- works under direct supervision of plant engineer
- performs a variety of technical duties necessary to operate chemical plant
- makes limited contact beyond immediate associates
- errors could result in damage to plant equipment

Examples of Work -

- follow operational procedures as prescribed by plant operator;
be able to operate various sections of plant

Desirable Qualifications -

- High school graduate; 2 years technical training; 5 years experience as chemical technician; or any equivalent combination of education and experience

Assistant Operator

Definition - skilled technical work in connection with the operation of chemical plant

Distinguishing Characteristics -

- works under direct supervision of chief operator
- performs duties, both complex and routine, necessary to operate chemical plant
- makes limited contact beyond immediate associates
- errors could result in damage to plant equipment
- physical effort required in event of plant breakdown

Desirable Qualifications -

- high school graduate; 2 years technical training; 2 years experience as chemical technician; or any equivalent combination of education and experience
- ability to understand and follow oral instruction

Equipment Operator (Receiving, Grinding, Landfill)

Nature of Work - performs skilled operation of refuse pulverizer as well as heavy equipment necessary for landfill operation

Examples of work -

- services equipment and makes field adjustments and repairs

Desirable Knowledge, Abilities and Skills -

- considerable knowledge of and skill in the operation, maintenance and use of refuse pulverization and heavy motor equipment
- operation of motor equipment over rough, icy and unstable surfaces
- knowledge of state and local laws concerning landfill of refuse
- knowledge of the occupational hazards involved and the safety precautions necessary to safely operate heavy motor and pulverization equipment

COSTS

Capital Cost

The total plant capital cost (TPCC) of the 36 ton per day facility has been estimated to be approximately \$1,100,000. The cost is based on a Marshall and Swift Cost Index of 326.8 and was calculated as follows: the purchased equipment cost (pec) of each piece of equipment was found from various sources (Table 32); installation costs were approximated as a factor of pec (Table 33); piping, buildings, engineering etc., were found by using factors of the installed equipment cost; the various costs were totaled to give the TPCC. These costs are broken down for the purpose of comparison with other systems. Since the feed preparation section represents established (not new, as the rest of the plant) technology it may be possible to find a similar system which can be operated at smaller cost.

The annual cost to operate the 36 ton per day plant is presented in Table 35. All of the possible natural gas applications have been replaced by product oil.

Table 32. PURCHASED EQUIPMENT COSTS (P.E.C.)

36 ton per day cellulose liquefaction plant

- 50% solid feed

Equipment	Purchased Equipment Cost	Footnote*
1. Heated slurry tank	\$6,400	1
2. Moyno pump	6,900	2
3. Furnace	23,800	3
4. Reactor	14,400	4
5. High pressure entrainment Separator	5,400	5
6. Liquid product heat exchanger	9,050	6
7. Continuous centrifuge	11,400	7
8. Product oil pump	750	8
9. Sludge pump	750	8
10. Gas heat exchanger	14,300	6
11. Condenser I	23,000	9
12. Condenser II	1,150	9
13. Low pressure entrainment separator	300	5
14. Large compressor	16,350	10
15. Condensate pump	750	8
16. Product storage tank	4,100	11
17. Small compressor	12,800	10
18. Storage oil heat exchanger	700	6
19. Water storage tank	2,800	11
20. Boiler	4,100	13
21. Adsorption towers (2)	10,600	1

(pec) continued

	<u>cost</u>	<u>footnote</u>
22. Settling tank	7,900	1
23. Precipitation tank	7,900	12
24. Pumps (3)	2,250	8
25. Gas storage tank	4,800	14
26. Spray pond	2,500	15
27. Cooling system pump	1,000	8
28. Air compressor	<u>5,500</u>	13
Total	\$201,650	

*Footnote refers to source of each price.

Table 33. PLANT COSTS^a

Factor	Cost
Purchased equipment cost (pec)	\$201,650
Installation (.50 pec)	100,825(A=302,475)
Piping (.50A)	151,237.5
Instrumentation (.10A)	30,247.5
Engineering (.50A)	151,327.5
Building (outside construction)(.20A)	60,495
Auxiliary facilities*(.25A)	75,618.75
Outside lines (.10A)	30,247.5
Startup (.10A)	30,247.5
Subtotal	831,806.25
Packaged hydrogen plant	98,500
Packaged hydrogen recovery	67,500
Receiving and grinding area**	119,100
PLANT COST	\$1,116,906.25

*includes:

compressor oil recovery system
 flare stack
 communications systems
 loading racks
 toilet facilities
 hydrocarbon recovery system for oil
 storage tanks, etc.

**broken down as follows:

refuse conveyor 4200
 pre-grinder storage 5400
 hammermill & feed
 conveyor 80,000
 mechanical air
 separator 15,000
 storage silo 13,000
 screw 1,000
 elevator 500
 119,100

^a36 ton per day cellulose liquefaction plant

- 50% solid feed

Table 34. FEED PREPARATION COSTS

Machinery repair/replacement	\$.60/ton
Utilities (electricity) cost*	.15/ton
Labor and benefits**	.98/ton
Total	\$1.73/ton

$$*115 \text{ hp} \times \frac{8 \text{ hr}}{\text{day}} \times .746 \frac{\text{Kw}}{\text{hp}} = \frac{685 \text{ Kwh/day}}{36 \text{ tons/day}} = 19 \frac{\text{Kwh}}{\text{ton}} \times .008 \frac{\$}{\text{Kwh}} = .15 \frac{\$}{\text{ton}}$$

$$**1 \text{ equip. operator} \times \$8,000/\text{year} + 10\% \text{ benefits} = \$8800/\text{year}$$

$$\frac{\$8800/\text{year}}{2000 \text{ hrs/year}} = 4.4 \text{ \$/hr}$$

$$\frac{4.4 \text{ \$/hr}}{4.5 \text{ tons/hr}} = .98 \text{ \$/ton}$$

Source: Francis and John S. Lane Limited, England, manufacturers of
Lanvay Refuse Pulverizers

Table 35. ANNUAL OPERATING COSTS^a

	Annual Amount	Annual Cost
Utilities		
Electricity	1.10 x 10 ⁶ KWH at .008\$/KWH	8,800
Oil	4.2 x 10 ³ Bbl	----
Chemicals		
Catalyst	3.75 x 10 ⁴ lb.	18,000
Activated carbon	1.00 x 10 ⁴ lb.	5,000
Labor		
Labor*		95,500
Benefits**		9,550
Other		
Materials and supplies (includes maintenance supplies)		100,000
10% amortization of capital cost		<u>110,000</u>
Total Annual Operating Costs		\$346,850

	Total	Annual Salary	Total Cost
*Labor			
Chief operator (1 per shift)	3 at	10,000	30,000
Asst. operator (1 per shift)	3	8,000	24,000
Engineer (on call at night)	1	15,000	15,000
Maintenance (on call at night)	1	10,000	10,000
Secretary	$\frac{1}{2}$	5,000	2,500
Equipment operator	1	8,000	8,000
Quality control chemist	$\frac{1}{2}$	12,000	<u>6,000</u>
			\$95,500

**10% Benefits, \$9,550

36 tons per day cellulose liquefaction plant

- 50% solid feed

- 260 operating days per year (24 hrs/day)

Economics of Scale

Economic projections, carried out by scaling up the costs associated with this 36 ton per day plant, show that a plant with a capacity as small as 1000 tons refuse/day could break even if the product (a low oxygen, high heating value oil) sells for as low as \$4.75/BBL. The profitability of the process as a function of plant size is shown in Figure 62 where % return on investment is plotted as a function of product oil price.

The following assumptions were used in the calculations of these economic projects.

1) Production of oil - the net yield of oil per ton of combustible refuse is calculated to be 2.15 BBL. Combustible refuse is defined as "raw" municipal refuse minus ash, metal, and glass (includes moisture). This yield is calculated from pilot plant data.

2) Because the plants are highly automated the personnel required to operate the various sized plant is considered to be the same.

3) Capital costs were scaled up from the 36 ton per day plant via the "six-tenth rule", and that amortization of capital costs was taken over a 10 year period in each case.

The cost versus capacity figures are presented in Table 36.

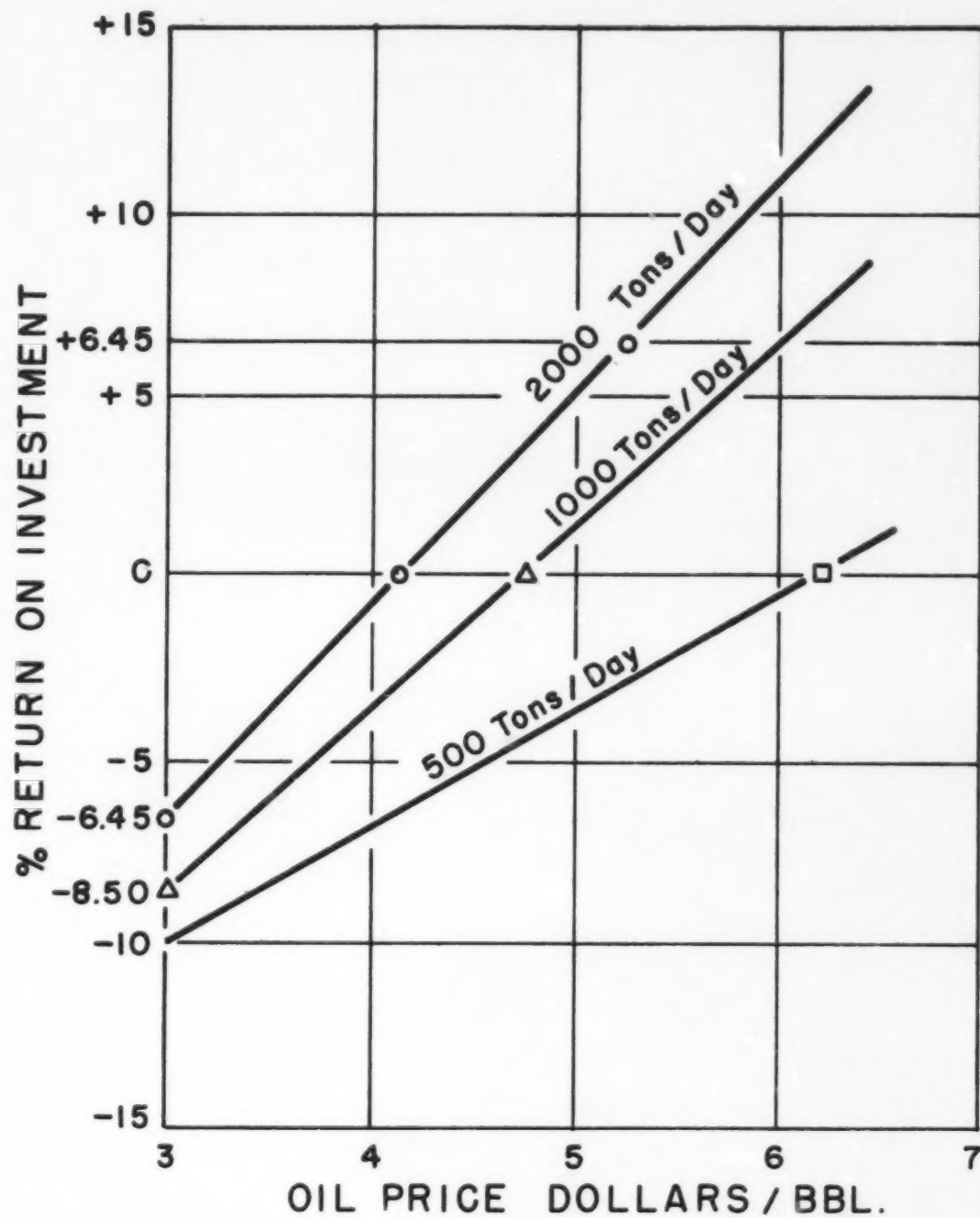


Figure 62

Table 36. COST VS. CAPACITY^a

Tons/day	Capital Cost	Annual Operating Cost	Net Annual Production ^b Bbl/year	Gross Cost of Production \$/BBL
5	\$341,000	\$243,000	2000	121.50
10	517,000	265,000	4000	66.25
36	1,116,900	346,850	14000	24.77
100	2,060,000	498,000	40000	12.45
500	5,420,000	1,185,000	200000	5.92
1000	8,200,000	1,900,000	400000	4.75
2000	12,400,000	3,200,000	800000	4.00

^abased on 260 operating days/year (5 days/week)

^bbased on 2.15 BBL/ton

ENVIRONMENTAL IMPACT

In any petrochemical plant many possible sources of pollution exist. This is also true for the solid waste liquefaction plant. Such sources include: 1) Thermal Pollution (the heating from water used as cooling water in processes), 2) Noise Pollution (the noise created by the hammer-mill), 3) Air Pollution (the releasing of gases to the atmosphere), 4) Water Pollution (the presence of phenols and other organics in the acidic waste water product of the cellulose conversion reaction) and 5) Ground Water Pollution (the leaching into the ground of any unreacted solids and catalyst which might be present in the landfilled sludge). However, the plant has been designed to have no adverse effect on the environment. Each of the possible sources of pollution will be outlined below and the steps taken to correct them will be discussed.

Thermal Pollution

The possibility of thermal pollution has been eliminated in two ways: 1) the need for cooling water has been reduced by waste heat recovery within the plant and 2) a spray pond has been designed to cool the cooling water that must be used. No hot water will be released to the environment.

Noise Pollution

The refuse pulverizer (hammermill) is the main source of noise within the plant. It is expected that this noise will not cause any problems because: 1) the hammermill will be located far away from the population center of the plant (control room), and 2) the area in which the plant is to be built is a sparsely populated area. Thus, no disturbance of residents is expected.

Air Pollution

Gases formed in the reaction include CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , CO , CO_2 . Since the mixture has a good heating value, it will be used in the furnaces and boilers throughout the plant. CO_2 will be released to the air.

Water Pollution

The water produced in the reaction has organics mixed with it, therefore it cannot be put out to the environment as is. Physically, it looks brown, smells phenolic and has a pH of close to 2. However, by treatment with activated carbon, these organics are removed. Absorption on activated carbon has long been recognized as a valid method for the treatment of water.

Ground Water Pollution

Experiments to date show that inorganics put into the process (catalysts and others from refuse) come out of the process as a sludge. The sludge is landfilled. Since it is sterile, it does not contribute to ground water pollution.

Environmental Benefits

The plant will conserve available landfill sites by reducing the volume of solid waste to about 20% of their initial volume. Also, the ground water pollution problems based by leachates from landfill will be halted.

QUESTIONS AND ANSWERS - INTERACTION

The following questions have been prepared by the townspeople and officials of the Town of Holden, Massachusetts, regarding the erection of a Solid Waste Liquefaction Plant. Their questions and our answers to those questions form an important foundation for cooperation and understanding. Additionally, the points raised are of general interest and provide critical insight to the types of problems that will result in implementing a municipal scale solid waste liquefaction process in its first scale-up.

A. Question: Statement of Purpose of Building and Operating Proposed Conversion Plant in Holden.

Answer: The plant will be operated as an experimental facility for approximately three years, during which time the following should be completed: Final characterization of products, optimization of plant operation, stabilization of product quality, and collection of data for use during scale up. The overall result of the development stage would be to optimize the process while simultaneously processing Holden's combustible refuse.

The post-development operation could proceed for other proposed installations. This would involve optimization of operating conditions for the various feed stocks available. The second method of utilization would be as part of the Massachusetts State Regionalization Program. The liquefaction plant could be used as a partial solution to the solid waste problems of the Worcester Region.

B. Physical Plant

B-1 Question: What is the size of the plant (outside dimensions)?

Answer: The plant has outside dimensions of 150' x 150' (See Fig. 61).

B-2 Question: How large a land area is required for this plant?

Answer: The plant will require 200' x 200' plus access road.

B-3 Question: What will be the outside physical appearance of it?

Answer: It will look like a petroleum refinery, only on a much smaller scale.

B-4 Question: What is the maximum physical capacity of refuse converted per day for which the plant is designed?

Answer: The plant will convert approximately 36 tons/day of dry refuse.

B-5 Question: Will the proposed size be adequate to handle more than just Holden's waste production?

Answer: This size plant will be able to handle Holden and West Boylston refuse for at least 15 year if expanded to seven day operation.

B-6 Question: Where is the plant to be located?

Answer: At the sanitary landfill in Holden - Area D which is in reserve for future use.

B-7 Question: How much storage capacity will there be for refuse which is to be converted?

Answer: Since most of a week's refuse arrives at the plant on Saturday or Sunday, much storage capacity has been designed in the form of the pre-shredder storage (50 cy), storage silo (285cy) and surge tank (40cy). (cy = cubic yards)

B-8 Question: What is the physical capability to expand the plant?

Answer: Capacity can be expanded if operation is extended to seven days per week, 48 weeks per year, giving approximately 30% greater capacity.

C - Plant Operation

C-1 Question: How many hours per day and days per week will the plant initially operate.

Answer: The plant will initially operate 24 hours per day on a 5 day per week basis.

C-2 Question: What quantity of refuse per day will it initially handle?

Answer: Initially the plant will handle sporadic amounts of refuse until startup problems are eliminated.

C-3 Question: If Holden continues to grow at its forecasted rate, in how many years will the plant reach its maximum physical capacity?

Answer: The plant has the capability to handle Holden's waste until the year 1990.

C-4 Question: What type and number of personnel will be required to operate the plant initially?

Answer: During initial operation and development, the personnel will include both a WPI developmental team and an operational staff.

C-5 Question: After initial experimental stage (1 to 2 years), how many men will be needed to operate the plant?

Answer: The personnel necessary per typical year of operation are listed on page 173.

C-6 Question: Who will be held responsible for the proper operation of the plant?

Answer: The engineer is the man in charge of the plant.

C-7 Question: What qualifications must plant operators and technicians possess?

Answer: They must be skilled chemical technicians.

C-8 Question: Specifically what wastes will not be handled by the plant?

Answer: Metals, glass, stones, tires (grinding problems), oversized materials such as tree stumps and construction or wrecking refuse.

C-9 Question: What size limitations will there be on allowable wastes?

Answer: Under 12" x 12" x 12"

C-10 Question: Will the landfill continue to require daily operation?

Answer: Yes- metal cans, glass, etc., which are not recycled must be landfilled as well as unconverted waste (3,000 lb/day) from the plant.

C-11 Question: Will all refuse be landfilled when the plant is down?

Answer: Yes

C-12 Question: What portion of wastes currently landfilled will continue to be landfilled?

Answer: Approximately 25% by weight (10% by volume) is considered to be metal cans, glass; however, recycling operations could eliminate much of this.

C-13 Question: How many years of life will the landfill have under the proposed system?

Answer: Approximately 20% of existing refuse volume will need to be landfilled. The landfill, which had a life expectancy of 18 years under the old system, could last for 90 years at the present refuse production rate.

C-14 Question: What amount and type of catalyst will be used?

Answer: Approximately 6 lb/hr of Nickel Cat.

C-15 Question: What properties does the oil by-product possess (chemical analysis)?

Answer: Oxygen free, low sulfur, heating values from 16,000-19,000 Btu/lb.

C-16 Question: List all specific uses to which this oil can be put in its crude state.

Answer: Heating homes (schools, etc.), refinery feed, blending with high sulfur oils, etc.

C-17 Question: How consistent in chemical composition will the oil be?

Answer: The product will be quite uniform in spite of the wide variations in the nature of solid waste.

C-18 Question: How much oil per ton of refuse will be produced?

Answer: 2.25 Bbl oil/ton refuse.

C-19 Question: Can sewage sludge be processed?

Answer: The plant will operate with ease on sewage sludge.

C-20 Question: How much down time is expected (range)?

Answer: Two days per week, or if the plant is expanded to 7 days/week, 4 WKS per year after development stage.

C-21 Question: What economics of scale might exist for this type of plant?

Answer: Please see economics section. Larger plants show a profit.

D - Collection

D-1 Question: Will the building of the plant in any way affect the manner of waste collection in Holden?

Answer: Yes. The waste will need to be separated, i.e., only combustibles will be used in the plant.

D-2 Question: Which is the most efficient and least costly method of collection and transportation of refuse to the site?

Answer:

D-3 Question: What is the opinion of the residents of Holden towards collection vs. individual transporting of refuse?

Answer:

D-4 Question: Will waste materials need to be separated?

Answer: Yes, in order to protect equipment.

D-5 Question: Will separation be done by private residents or within the plant?

Answer: Can be done either way but separation by residents will minimize plant capital cost.

E. Utilities

E-1 Question: If a well is developed near the site, how much water would be available (maximum)?

Answer: The test well proved negative.

E-2 Question: If water is extensively recycled within the plant, what is the minimum amount that would be required for operation?

Answer: 5 gpm.

E-3 Question: How much electricity will the plant require?

Answer: 3300 KWH/day.

E-4 Question: What are the natural gas needs of the plant?

Answer: 2930 ft³/hr.

E-5 Question: Can these needs be serviced by storage tanks on the site or must a gas line be extended to the site?

Answer: Storage tanks will be fine as this gas will only be used until the plant is stabilized and our own gas will be used.

F Environmental

F-1 Question: Will the plant be noisy?

Answer: Yes, the grinder is noisy. It is scheduled to operate on the day shift only.

F-2 Question: Will it smell?

Answer: The product has an odor. Barring spills and with good housekeeping the plant will be relatively odor free.

F-3 Question: Will it pollute the air?

Answer: No, only clean burning fuels are used, and technology regarding this is high.

F-4 Question: Will it pollute the water?

Answer: No, we only heat the water we use.

F-5 Question: Will the plant cause more traffic on the roads leading to the site thereby disturbing residents along these roads?

Answer:

F-6 Question: Is there any explosion danger?

Answer: Safety in petroleum refineries, where gases and fuels are processed at elevated temperatures and pressures, is always a prime consideration. The industry record is excellent and we would also conform to the reliable principles and practices of the petroleum industry.

G-3 Question: Specifically what government agency or agencies will finance the project?

Answer:

G-4 Question: What potential for revenue exists such that the plant may become economically self-sustaining or profit-making after it is dropped as a pilot project?

Answer: The economics for operation without government subsidy do not look favorable because of the small size of this plant. It is a process development facility.

H. Administrative and Legal

H-1 Question: What is WPI's role in the proposal?

Answer: To supply technical expertise, personnel, and assume the management responsibility.

H-2 Question: What is Holden's role in the proposal?

Answer: To provide segregated solid waste, landfill of process solid sludge and unprocessed material, to use the oil at market value and to provide the plant site.

H-3 Question: Who bears ultimate responsibility in this project - WPI? Holden? both jointly?

Answer: The plant will be used to provide the basis for the solution to the solid waste problems of District 5-3. It will provide the data and experience for a highly optimized, fail-safe regional plant design.

H-6 Question: Are there any legal complications associated with the sale of petroleum products by a town to a private industrial firm?

Answer: The town should endeavor to use the oil itself to maximize revenue. If oil is to be sold, it should be through established commercial vendors, the town landfill assuming the role of an oil well.

I. Miscellaneous

I-1 Question: What role will the plant play in Holden's waste disposal system in the period after the development and experimental work is completed?

Answer: Completely take care of the town refuse disposal until 1990. It is expected that process improvement and feed stock testing programs will continue on a sustained basis. These would justify and support continued operation.

I-2 Question: List all direct and indirect benefits to the citizens of Holden which are attained by the pursuit of this project (include costs wherever possible).

Answer:

I-3 Question: List all advantages to Federal government agencies, the Central Massachusetts Region and other communities obtained from this pilot project.

Answer: The process will be proven on a realistic scale, permitting scale up with confidence to 1000 ton/day and larger across the nation. It will ultimately establish solid waste as a resource of value in the nation, and change the solid waste expense problem to a break-even or profitable operation.

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